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A
COMMENTARY
ON THE SCIENTIFIC WRITINGS OF
J. WILLARD GIBBS

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PHYSICS IN YALE UNIVERSITY

IN TWO VOLUMES

I. THERMODYNAMICS

DEALING WITH THE CONTENTS OF VOLUME ONE
OF THE COLLECTED WORKS

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FOREWORD

These volumes have been prepared with a two-fold purpose,—to honor the memory of J. Willard Gibbs, and to meet what is believed to be a real need. They are designed to aid and supplement a careful study of the original text of Gibbs' writings and not, in any sense, to make such a study unnecessary.

The writing and printing of this commentary have been carried out under the auspices of Yale University, and have been financed in part from University funds and in part by generous contributions received from Professor Irving Fisher of Yale, to whom credit is also due for having conceived and initiated the movement for a memorial to Willard Gibbs of which this commentary is the direct and, thus far, the principal result.

In January, 1927, an informal meeting was held of members of the Yale faculty interested in the creation of such a memorial. The proposal to publish a commentary on Gibbs' writings met with favor, and a committee was appointed to study the matter. After an extended investigation, in the course of which personal opinions were obtained from a large number of authorities, both in this country and abroad, on the desirability of such a commentary and on various questions of policy, the committee reported favorably, and was thereupon instructed to carry the plan into effect. Definite arrangements were completed in February, 1929, and work began during that year, but it was not until four years later that the manuscript of both volumes was ready for the press.

Each of the two volumes deals with the portion of Gibbs' writings contained in the like-numbered volume of *The Collected Works of J. Willard Gibbs.* Volume I, "Thermodynamics" is essentially interpretative and explanatory, but includes a discussion of recent developments concerning Gibbs' thermodynamic principles and many examples, drawn from the modern literature, of their application to concrete problems.

Volume II, "Theoretical Physics", contains an analysis, appreciation and interpretation of Gibbs' work in this field, especially his statistical mechanics, and, in addition, a discussion of the relation of Gibbs' statistics to the modern quantum statistics. The volumes are separately indexed and except for a few cross-references are entirely independent of each other.

May this commentary, the product of devoted and conscientious labors on the part of its authors and editors, prove truly helpful to those who wish to follow the paths opened up by Willard Gibbs, and promote a better and more widespread appreciation of the value of his services to science.

The Committee on the Gibbs Commentary
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RALPH G. VAN NAME, *Chairman*

Yale University
May, 1936

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PREFACE TO VOLUME I

The present Volume of the Commentary deals with Gibbs' thermodynamical papers, and principally with the famous paper on *The Equilibrium of Heterogeneous Substances.* In this immortal work, Gibbs, building on the sure foundations laid by Carnot, Mayer, Joule, Clausius and Kelvin, brought the science of generalised thermodynamics to the same degree of perfect and comprehensive generality that Lagrange and Hamilton had in an earlier era brought the science of generalised dynamics.

The originality, power and beauty of Gibbs' work in the domain of thermodynamics have never been surpassed. The generality and abstract nature of the reasoning have, however, made the understanding of his methods and results a difficult task for many students of science. This has been particularly true of students of chemistry, who in general are deficient in mathematical training and are not as a rule familiar with the methods and results of generalised classical dynamics—a very necessary mathematical precursor to the study of generalised thermodynamics. This state of affairs has been very unfortunate in the past, since the work of Gibbs contained a complete and perfect system of chemical thermodynamics, i.e., a system of thermodynamics peculiarly well adapted to the most general and complete application to chemical problems. What, for example, could exceed, in simplicity and generality, Gibbs' expressions, in terms of his *chemical potentials*, for chemical equilibrium in a homogeneous phase or the distribution equilibrium of independent components throughout a system of coexistent phases?

Although the physicist will undoubtedly find much of the greatest interest and value in the present volume, this Commentary is intended for the use of students of physical chemistry as well as physics. The Articles contained in it are not therefore merely running comments on and illustrations of Gibbs' equations, but constitute in each case a thoroughgoing discussion of the corresponding part of Gibbs' work, the object of which is so to smooth the path for the reader of the original papers that the methods and results of Gibbs will be intelligible to and available for the use of all serious students of both chemistry and physics. The only exception to this mode of treatment will be found in the interesting Article C of the present volume, where our distinguished collaborator, Professor E. B. Wilson, considered it more advantageous to give an outline of Gibbs' own lectures on thermodynamics than a detailed discussion of Papers I and II of Volume I of *The Collected Works of J. Willard Gibbs.* Readers who have followed the reasoning given by Gibbs in his lectures will find no difficulty in understanding the graphical developments of Papers I and II.

In order further to lighten the work of the mathematically inexpert reader, the present volume contains a short Article (B) dealing with certain mathematical methods. In this connection reference may be also made to Chapter II of the Special Commentary on Gibbs' Statistical Mechanics by A. Haas, dealing with the algebra of determinants and contained in Volume II of the Commentary. One of the objects of Article F of the present Volume is to familiarise students with certain mathematical difficulties, e.g. the difference between Gibbs' use of the operators δ and Δ.

Some points of detail may now be considered. In the Table of Contents and in the titles of the Articles of the present Volume, the expression "Gibbs, I, pp." refers to the relevant part of Volume I of *The Collected Works of J. Willard Gibbs* (two volumes), Longmans, Green, and Co., 1928, or to the like-numbered volume and page of *The Scientific Papers of J. Willard Gibbs,* Longmans, Green, and Co., 1906.* This applies also to occasional references in the text. In each Article the current numbers referring to the particular author's equations are given between *curved parentheses,* whereas the numbers referring to the equations as given by Gibbs in the original paper are enclosed between *rectangular brackets.* When coincidence occurs, as is very frequently the case, the necessary *double numbering* is given, e.g. Equation . . . . . . (a) [g]. Here *a* is the author's number, *g* is Gibbs' number. The same method is followed in the reference numbers of equations given in the text.

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* The *Collected Works* is a reprint of the *Scientific Papers,* with identical pagination and contents except that it includes (in Volume II) Gibbs' *Elementary Principles in Statistical Mechanics,* which was not printed in the *Scientific Papers.* References to this particular portion, however, occur in this Commentary only in Volume II and in Article J of Volume I.

The notation employed by Gibbs for the principal thermodynamic quantities has been retained in general, the few deviations from this procedure being indicated at the appropriate places in the text. In order to facilitate comparison with the usage of a number of other writers on thermodynamics, a comparison Table of Symbols is given (Article A). This Article also contains a comparison Table of the names assigned to the principal thermodynamic quantities by Gibbs and a number of other writers.

Of the Articles contained in this Volume, all, with the exception of A and C, refer to Paper III of Volume I of the *Collected Works*, i.e., the paper on *The Equilibrium of Heterogeneous Substances,* and Papers (Sections) V, VII, VIII, and IX. Article D deals with the general thermodynamic system of Gibbs, as expounded in Gibbs, I, pp. 55–144; 419–424. Special parts of this section of Paper III are further discussed and illustrated in Articles E, F, G, and H, whilst Articles I, J, K, L and M deal with the remaining portions of Paper III (and Sections V, VII, VIII and IX) of Volume I of the *Collected Works.*

Readers of this Volume will find in Volume II of the Commentary a general survey of Gibbs' thermodynamical methods and results (by A. Haas), as well as an account of certain subsequent work (by P. S. Epstein).

In the present Volume we have not dealt with such later developments as the Nernst Heat Theorem and related topics, since a proper understanding of the present state of this subject requires a considerable knowledge of Statistical Mechanics. These matters are dealt with by P. S. Epstein in Volume II of the Commentary.

Besides the condensed survey of Gibbs' thermodynamical methods and results contained in Volume II of the Commentary, students will find an excellent account in the book of E. A. Guggenheim, entitled *Modern Thermodynamics by the Methods of Willard Gibbs* (Methuen & Co., London, 1933).

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The thermodynamical writings of Gibbs have proved a golden source of knowledge and inspiration to later workers. This mine is by no means exhausted. It is the confident belief of the Editors that those who are led by the present book to a study of the relevant parts of Gibbs' work will find therein much that is as yet imperfectly understood and experimentally undeveloped. Gibbs was no mere generaliser of the work of others, but a profound and original investigator who opened new domains of knowledge to the mind of man.

As is well known, Gibbs himself endeavored to obtain a *rational* foundation for thermodynamics in his splendid development of the science of Statistical Mechanics, founded by Clerk Maxwell and Boltzmann (see Volume II of the Commentary). Nowadays, by means of the quantum concept and the newer methods of theoretical physics, the older Statistical Mechanics has been transformed into a new science of Quantum Statistics and Quantum Mechanics. Although without doubt this wonderful new development penetrates much more deeply into the analysis of the phenomenal world than the older science of thermodynamics, there is no reason to deny the term *rational* to the earlier method. It deals with the phenomenal world in a different manner, but it remains, within its rightful domain, an enduring and powerful weapon of the human mind. Moreover, the modern development of physical theory tends more and more to revert to the essential *method of thermodynamics,* which abstains from "mechanical" pictures of individualised entities interacting in space and time, and describes phenomena by means of a generalised functional analysis. Thermodynamics was indeed the essential precursor of the modern method. It will ever be the imperishable achievement of Gibbs to have developed this earlier scientific method to the fullest extent of its power.

Modern physical chemistry utilises in constantly increasing measure the newer developments of theoretical physics. Nevertheless, thermodynamics is one of the principal foundations on which the structure of "classical" physical chemistry rests. Every well-trained student of pure or applied chemistry must therefore possess a thorough working knowledge of its principles and methods. In this essential task he will find no surer or better guide than the original papers of J. Willard Gibbs.

In the work of producing this Commentary we have been fortunate in enlisting the cooperation of a number of very able collaborators, to each of whom has been entrusted a special section of the Volume. To all these collaborators we desire to express our very high appreciation of the work which they have accomplished.

Our work as Editors has been greatly lightened by the extreme care which the members of the Gibbs Committee have bestowed on the correction of the proofs and on many other matters of importance. For this valuable help we are extremely grateful.

Last, but not least, we wish to express, on behalf of ourselves and our collaborators, our deep sense of the honor which the Gibbs Committee has conferred upon us all. Should our joint labors succeed in liberating the beautiful work of Gibbs from the abstract *tour d'ivoire* in which it has been for so long concealed from many students of science, then great will be our reward.

London and Vienna,
January, 1936

F. G. Donnan
Arthur Haas

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A

NOTE ON SYMBOLS AND NOMENCLATURE

F. G. DONNAN

In the following Commentary on the thermodynamic writings of J. Willard Gibbs the symbols used by him for the principal thermodynamic quantities have been retained in general. Since the majority of authors have employed symbols which differ considerably from those of Gibbs, and the notation employed varies in some respects from author to author, a short comparison Table is given below. There has also existed, and indeed still exists, a very considerable variation of usage as regards the names assigned to some of the quantities. It has therefore been thought desirable to give a correlated list of the principal names which are, or have been, employed. We shall denote six important thermodynamic quantities by the numerals 1, 2, 3, 4, 5, 6. The symbols assigned to these six quantities by Gibbs and

TABLE 1
Comparison of Symbols

Author	Thermodynamic quantities					
	1	2	3	4	5	6
Gibbs	t	ϵ	η	χ	ψ	ζ
Massieu	T	U	S	U'	$-T\psi$	$-T\psi'$
Helmholtz	θ	U	S	—	H	—
Duhem	T	U	S	—	F	Φ
Planck	T	U	S	W	F	$-T\Phi$
Lewis and Randall	T	E	S	H	A	F
Lorentz	T	ϵ	η	χ	Ψ	ζ
Noyes and Sherrill	T	U	—	H	A	F
Partington	T	U	S	H	F	Z
Schottky, Ulich and Wagner	T	U	S	H	F	G
Sackur	T	E_v	S	E_p	F_v	F_p
Guggenheim	T	E	S	H	F	G

various authors are shown in Table 1, whilst the corresponding names are given in Table 2.

TABLE 2

NAMES OF QUANTITIES

Quantity	Names employed
1	Absolute Temperature. Temperature on the Kelvin (thermodynamic) scale.
2	Energy. Total internal Energy.
3	Entropy.
4	Total Heat (term used by engineers). Heat Function for constant pressure (Gibbs). Heat Function (Partington; Sackur; Milne). Heat Content (Lewis and Randall; Noyes and Sherrill). Enthalpy (Kamerlingh Onnes).
5	Available Energy (Clerk Maxwell). Free Energy (Helmholtz). Isothermal Potential (Helmholtz). Internal Thermodynamic Potential (Duhem). Free Energy (Planck; Lorentz; Sackur; Partington; Schottky, Ulich and Wagner; most European authors since Helmholtz). Work Content (Noyes and Sherrill). Work Function (Milne). Helmholtzian Free Energy (Guggenheim).
6	Thermodynamic Potential at constant Pressure (Duhem). Free Energy (Lewis and Randall; Noyes and Sherrill; many authors, American and European, following the lead of the American School of chemical thermodynamics created by Noyes and Lewis). Thermodynamic Potential (Lorentz; Sackur; Partington). Gibbs' Thermodynamic Potential (Schottky, Ulich and Wagner). Gibbs' Free Energy (Guggenheim).

Notes to Tables

(a) Gibbs, using ψ to denote 5, called $-\psi$ the "Force Function for Constant Temperature."

(b) Massieu called his functions ψ and ψ' the "Characteristic Functions" of the system.

(c) It will be noted that Planck's function Φ is identical with Massieu's function ψ'.

(d) As regards nomenclature used at the present time, it is to be noted that *both* the quantities 5 and 6 are called Free Energy. This is a source of confusion to students of thermodynamics. Similar remarks apply to the use of the symbol F, which may denote either 5 or 6.

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B

MATHEMATICAL NOTE

JAMES RICE

1. The Method of Variations Used for Determining the Conditions under Which a Function of Several Variables Has a Maximum or Minimum Value. In the discussion of the conditions for equilibrium of a system and of the criteria of stability of a state of equilibrium, the following mathematical problem is presented:

To determine the values of the variables $x_1, x_2, \ldots . x_n$ for which a given function of these variables, $f(x_1, x_2, \ldots . x_n)$ has a maximum or minimum value, the variables themselves being subject to a condition such as

$$\phi(x_1, x_2, \ldots . x_n) = 0,$$

where ϕ is another given functional form.

Considering a definite set of values for the variables, say $x_1 = q_1$, $x_2 = q_2, \ldots . x_n = q_n$ we compare the value of the function for this set with the value for any neighbouring set, such as $x_1 = q_1 + \delta q_1$, $x_2 = q_2 + \delta q_2, \ldots . x_n = q_n + \delta q_n$, where $\delta q_1, \delta q_2, \ldots . \delta q_n$ are infinitesimal quantities. These infinitesimal quantities are not completely arbitrary in their ratios to one another; for we have to choose them to satisfy the conditions

$$\begin{aligned} \phi(q_1, q_2, \ldots . q_n) &= 0, \\ \phi(q_1 + \delta q_1, q_2 + \delta q_2, \ldots . q_n + \delta q_n) &= 0. \end{aligned} \tag{1}$$

It is convenient to write for $\delta q_1, \delta q_2, \ldots . \delta q_n$ the symbols $\theta\xi_1$, $\theta\xi_2, \ldots . \theta\xi_n$ where θ is an infinitesimal positive magnitude whose value can be reduced without limit and $\xi_1, \xi_2, \ldots . \xi_n$ are finite quantities. The difference between the value of the function f for the set of values $(x_r = q_r)$ and the value for the set $(x_r = q_r + \delta q_r)$ is *

$$f(q_1 + \delta q_1, q_2 + \delta q_2, \ldots . q_n + \delta q_n) - f(q_1, q_2, \ldots . q_n).$$

---

* The enclosing bracket in $(x_r = q_r)$ or (q_r) indicates that we mean $x_1 = q_1, x_2 = q_2, \ldots . x_n = q_n$, or $q_1, q_2, \ldots q_n$.

By Taylor's theorem this is equal to

$$\sum_{r=1}^{n} \frac{\partial f(q)}{\partial q_r} \delta q_r + \frac{1}{2\,!} \sum_{r=1}^{n} \sum_{s=1}^{n} \frac{\partial^2 f(q)}{\partial q_r \partial q_s} \delta q_r \delta q_s + \text{etc.}$$

where we write $f(q)$ briefly for $f(q_1, q_2, \ldots . q_n)$. This difference we now write in the form

$$\theta \left\{ \sum_{r=1}^{n} \frac{\partial f(q)}{\partial q_r} \xi_r \right\} + \frac{\theta^2}{2\,!} \left\{ \sum_{r=1}^{n} \sum_{s=1}^{n} \frac{\partial^2 f(q)}{\partial q_r\, \partial q_s} \xi_r\, \xi_s \right\} + \text{etc.} \qquad (2)$$

As θ is reduced in value, the numerical magnitude of the term in θ preponderates more and more over the terms in $\theta^2, \theta^3, \ldots .$ (apart from discontinuities arising in the differential coefficients, a state of affairs which we cannot discuss here). The sign of this term will therefore determine whether $f(q + \delta q)$ is greater or less than $f(q)$. If $f(q + \delta q)$ is greater than $f(q)$ for any values of $(q_r + \delta q_r)$ consistent with the condition imposed, it is necessary that

$$\sum_{r=1}^{n} \frac{\partial f(q)}{\partial q_r} \xi_r = 0 \qquad (3)$$

for any possible sets of values of (ξ_r), since if the expression on the left-hand side of (3) were positive for a set of values of (ξ_r), it would be negative for the set with opposite signs, and so $f(q + \delta q)$ would not be greater than $f(q)$ for all possible sets of $(q_r + \delta q_r)$. If the quantities (ξ_r) were perfectly arbitrary this would necessitate the n conditions, $\partial f(q)/\partial q_r = 0$. However, they are not arbitrary; for by (1) they satisfy the condition

$$\sum_{r=1}^{n} \frac{\partial \phi(q)}{\partial q_r} \xi_r + \frac{\theta}{2\,!} \left\{ \sum_{r=1}^{n} \sum_{s=1}^{n} \frac{\partial^2 \phi(q)}{\partial q_r\, \partial q_s} \xi_r\, \xi_s \right\} + \text{etc.} = 0.$$

For very small values of θ, this becomes

$$\sum_{r=1}^{n} \frac{\partial \phi(q)}{\partial q_r} \xi_r = 0. \qquad (4)$$

Suppose we multiply (3) by $\partial\phi(q)/\partial q_1$, (4) by $\partial f(q)/\partial q_1$ and subtract (4) from (3) we obtain

$$\sum_{r=2}^{n}\left\{\frac{\partial f(q)}{\partial q_1}\cdot\frac{\partial\phi(q)}{\partial q_r}-\frac{\partial\phi(q)}{\partial q_1}\cdot\frac{\partial f(q)}{\partial q_r}\right\}\xi_r = 0. \qquad (5)$$

Now we can certainly choose the $n - 1$ quantities $\xi_2, \xi_3, \ldots. \xi_n$ in an arbitrary fashion, since on choosing a set we can adjust the value of ξ_1 to satisfy (4). It follows that in order to satisfy (5) for any values of $\xi_2, \xi_3, \ldots. \xi_n$ the following relations must be true:—

$$\frac{\partial f(q)}{\partial q_1}\bigg/\frac{\partial\phi(q)}{\partial q_1}=\frac{\partial f(q)}{\partial q_2}\bigg/\frac{\partial\phi(q)}{\partial q_2}=\ldots.=\frac{\partial f(q)}{\partial q_n}\bigg/\frac{\partial\phi(q)}{\partial q_n}, \qquad (6)$$

since they make all the coefficients of $\xi_2, \xi_3, \ldots. \xi_n$ in (5) individually zero.

Exactly the same argument shows that if the function $f(x_1, x_2, \ldots. x_n)$ has a minimum value for the set of values $(x_r = q_r)$ the same conditions (6) hold. It follows therefore that in order to determine the sets of values of the variables for which the function $f(x)$ is maximum *or* minimum in value, subject to the condition, $\phi(x) = 0$, we have to solve the n equations

$$\left.\begin{array}{c}\phi(x) = 0,\\ \dfrac{\partial f(x)}{\partial x_1}\bigg/\dfrac{\partial\phi(x)}{\partial x_1}=\dfrac{\partial f(x)}{\partial x_2}\bigg/\dfrac{\partial\phi(x)}{\partial x_2}=\ldots.=\dfrac{\partial f(x)}{\partial x_n}\bigg/\dfrac{\partial\phi(x)}{\partial x_n}.\end{array}\right\} \quad (7)$$

Any solution of these equations yields a set of values for "max-min" conditions.

A special case of this result, which is the one actually required for the considerations arising in Gibbs' *Equilibrium of Heterogeneous Substances*,* concerns the situation in which the condition imposed on the variables is that their sum should be a constant, i.e.

$$x_1 + x_2 \ldots. + x_n - c = 0.$$

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* See Gibbs, I, pp. 65 and 223.

In this case all the $\partial\phi(x)/\partial x_r$ are unity and equations (7) take the form

$$\phi(x) = 0,$$

$$\frac{\partial f(x)}{\partial x_1} = \frac{\partial f(x)}{\partial x_2} = \; \ldots\ldots \; = \frac{\partial f(x)}{\partial x_n}\,. \tag{8}$$

In order to distinguish between the sets of values which yield a maximum and those which yield a minimum, we must consider the terms in the expansion of $f(q + \delta q) - f(q)$ which involve θ and higher powers of θ. Thus we now write

$$f(q + \delta q) - f(q) = \frac{\theta^2}{2\,!}\left\{\sum_{r=1}^{n}\sum_{s=1}^{n} a_{rs}\,\xi_r\,\xi_s\right\}$$

$$+ \text{ higher powers of } \theta, \tag{9}$$

where a_{rs} is the value of the second differential coefficient $\partial^2 f(x)/\partial x_r\,\partial x_s$ when a set of values (q_r) obtained from the equations (7) are substituted for the variables (x_r). Now if this set of values yields a minimum, then the right-hand side of (9) must be positive for any possible values of ξ_r. If we now assume that the term in θ^2 preponderates in value over the remaining terms in θ^3, θ^4, etc. (which will be the case if the differential coefficients satisfy the usual conditions) then the condition for a minimum value is that the quadratic expression in (ξ_r)

$$a_{11}\,\xi_1^2 + a_{22}\,\xi_2^2 \;\ldots\ldots + 2\,a_{12}\,\xi_1\,\xi_2 + \;\ldots\ldots$$

should be positive in value for any set of values of (ξ_r) which satisfy the condition imposed. Actually the conditions which make the quadratic expression positive for any values of (ξ_r) *unrestricted by any condition* have been worked out by the mathematician; so these conditions will be *sufficient* for the criterion of minimum in our problem, though they may not be absolutely necessary for our restricted values. The conditions can be stated as follows. Consider the determinant of the nth order

$$\begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{vmatrix} .$$

Now consider:

(1) All the leading constituents $a_{11}, a_{22}, a_{33}, \dots a_{nn}$;

(2) All the minor determinants obtained by selecting any two rows and the *two corresponding* columns, for instance

$$\begin{vmatrix} a_{rr} & a_{rs} \\ a_{sr} & a_{ss} \end{vmatrix} ;$$

(3) All the minor determinants obtained by selecting any three rows and the three corresponding columns, for example

$$\begin{vmatrix} a_{rr} & a_{rs} & a_{rn} \\ a_{sr} & a_{ss} & a_{sn} \\ a_{nr} & a_{ns} & a_{nn} \end{vmatrix} ;$$

and so on;

(r) All the minor determinants obtained by selecting any r rows and the r corresponding columns;

and so on;

(n) The determinant itself.

If the quadratic expression is a "positive definite form," i.e. positive in value for all values of (ξ_r), then all the determinants in (1), (2), (3), ... (n) must be positive in value.

If on the other hand the set of values $q_1, q_2, \dots q_n$ for the variables $x_1, x_2, \dots x_n$ yield a maximum, then the quadratic expression in (ξ_r) must be a "negative definite form," i.e. negative in value for all values of (ξ_r). The conditions are that the determinants in (1), (3), (5), (7) etc. are all negative in value, while those in (2), (4), (6), (8), etc., are all positive.

If neither of these conditions holds, then the set of values $x_1 = q_1, x_2 = q_2, \dots x_n = q_n$ does not yield a true maximum or minimum condition and the consideration of the problem goes beyond the limits of possible discussion here.

For the proof of these results see any text of modern algebra, for example Bôcher's *Introduction to Higher Algebra*, Chapters IX–XII.

For reference to these conditions in the *Collected Works*, see Gibbs, I, pp. 111, 112, 242.

2. Curvature of Surfaces. The average curvature of a plane curve between two points A and B is defined as the quotient of the external angle between the tangents at A and B by the length of the arc AB. From a kinematic point of view it is the average rate of rotation of the tangent per unit length travelled by the point of contact. If the point B approaches indefinitely near to A, the limiting value of the average curvature is defined to be the curvature at the point A. In the case of a circle this is obviously the reciprocal of the radius at all points. For any curve at any point the curvature has the dimension of a reciprocal length, and so, on dividing the value of the curvature at a point on a curve into unity, we obtain a definite length which is then referred to as the "radius of curvature" at that point. Clearly where the curvature is relatively large the radius of curvature is relatively small; thus the extremities of the major axis of an ellipse are the points on it at which curvature is greatest but radius of curvature least; at the extremities of the minor axis, curvature is least, radius of curvature greatest.

The measurement of curvature at a point on a surface is based on this simple idea for a curve. Thus we conceive the tangent plane and the normal line to be drawn at a point P on the surface, and we then consider any line through P lying in this plane. An infinite number of planes can be drawn cutting the tangent plane in this line. These planes will cut the surface in an infinite number of curves, and we will readily recognise that sufficient information concerning the curvature of these curves at the point P will give us all the vital information concerning the curvature of the *surface* at P. Two obvious details in the construction of one such curve can be varied at will; we can alter the angle between the tangent plane at P and the plane drawn through the line in the tangent plane (the tangent line as we may call it) and we can alter the direction in the tangent plane of the tangent line.

In the first place a well-known theorem, known as Meunier's theorem, connects the radii of curvature of different sections through the same tangent line: the radius of curvature of an oblique section through a tangent line at P is equal to $R \cos \phi$ where R is the radius of curvature at P of the normal section, (i.e. the section containing the normal line at P as well as the tangent line) and ϕ is the angle between the normal section and the oblique section. Thus if we know the radius of curvature of the normal section through the chosen tangent line at P we implicitly know the radius of curvature of any given oblique section through it.

In the second place if we now vary the direction of the tangent line the radius of curvature of the normal section varies in a manner which is well known and quite simply described. Calling the curvature of the normal section c (where c is of course equal to R^{-1}) it is known that c varies continuously in value between a maximum limit and a minimum as the tangent line is rotated. It attains its maximum value twice in a complete rotation of the line, the two directions corresponding to this maximum being directly opposite to one another. The minimum is attained for the two opposite directions at right angles to the former. Taking the two lines thus marked out on the tangent plane as axial lines PX_1, PX_2 in the plane, we can indicate the direction of any other line in the tangent plane by the angle θ which it makes with PX_1, say. It is known that c, the curvature at P of the normal section through this line, is given by

$$c = c_1 \cos^2 \theta + c_2 \sin^2 \theta,$$

where c_1 and c_2 are the curvatures at P of the normal sections through PX_1 and PX_2. The values c_1 and c_2 are known as the "principal curvatures" of the surface at the point P. In this way we see that our complete knowledge concerning the curvature of a surface at a point P is summarized in a knowledge of the two principal curvatures at that point. One simple result of some importance follows very easily from the equation just written: if c and c' are the curvatures of two normal sections at a point which are at right angles to one another then $c + c'$ is a constant quantity at the point and is equal to $c_1 + c_2$.

On page 229 of Vol. I Gibbs uses an important theorem concerning the increase in size of a small portion of a surface produced by an elementary displacement of each element of the surface by an amount δN in the direction of its normal. Let the element of surface be $ABEF$ (Fig. 1) bounded by normal sections which are at right angles to one another. Let C be the "center of curvature" of the element AB of one of the sections, i.e., the position in the limit where the normals in the plane to the curve at the points A and B meet.* Let C' be the center of curvature

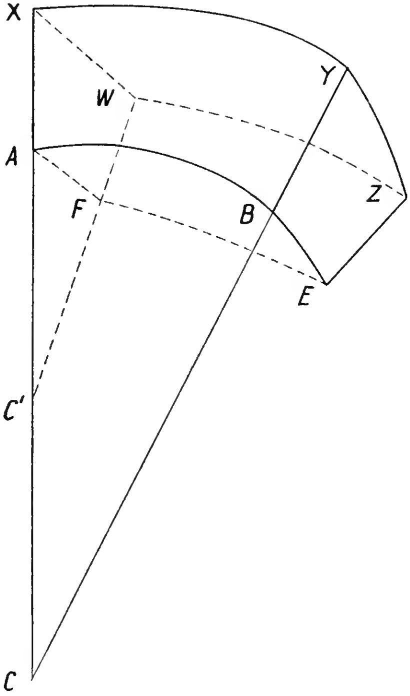

FIG. 1

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* The reader unacquainted with the geometry of surfaces is warned that for the sake of simplicity we have neglected a detail which is of no

of the arc AF in the other plane at A which is at right angles to the plane at ABC. Let the element of area be displaced to the position $XYZW$ where $AX = BY = EZ = FW = \delta N$. If the elementary angles $\angle ACB$ and $\angle AC'F$ are denoted by α and β then the area of the element of surface $ABEF$ is equal to the product of AB and AF, i.e., it is $R\alpha \times R'\beta$. If we denote this by s and the area of $XYZW$ by $s + \delta s$ we see that

$$s = RR'\alpha\beta,$$

$$s + \delta s = (R + \delta N)\,(R' + \delta N)\,\alpha\beta.$$

Therefore, neglecting products of the variations, we obtain the result

$$\begin{aligned}\delta s &= (R + R')\,\delta N\,\alpha\beta\\ &= s\,\frac{R + R'}{RR'}\,\delta N\\ &= s\left(\frac{1}{R} + \frac{1}{R'}\right)\delta N\\ &= s(c + c')\,\delta N.\end{aligned}$$

But since $c + c' = c_1 + c_2$ it follows that

$$\delta s = (c_1 + c_2)\,s\,\delta N,$$

a result used by Gibbs in obtaining equation [500]. It is used again on page 280 in the lines immediately succeeding equation [609] (where $\int \sigma\,\delta Ds$ is replaced by $\int \sigma(c_1 + c_2)\delta N Ds$) and also on page 316.

If the equation of a surface in Cartesian coordinates is given in the form

$$z = f(x, y)$$

---

importance for our purpose. But in order to avoid producing a wrong impression the writer must point out that if a plane section is drawn containing the normal to the surface at A, it is in general not true that the normal in this plane to the curve AB at B is also the normal *to the surface* at B. In our example where we are considering elementary arcs and areas of small size, this feature may be ignored without detriment to the argument.

the sum of the principal curvatures at a point x', y' z' on the surface can be calculated as follows: Let p and q represent the values of the differential coefficients $\partial f/\partial x$ and $\partial f/\partial y$ when the values x', y' are substituted for x, y, and let r, s, t be the values of the second differential coefficients $\partial^2 f/\partial x^2$, $\partial^2 f/\partial x \partial y$, $\partial^2 f/\partial y^2$ with the same substitutions; then

$$c_1 + c_2 = \frac{(1 + q^2)\, r + (1 + p^2)\, t - 2\, pqs}{(1 + p^2 + q^2)^{\frac{3}{2}}}.$$

This formula is used in obtaining equation [620] on page 283. Its proof will be found in any text of analytical solid geometry.

On page 293 of Gibbs, Vol. I, there is a reference to the *total* curvatures of the sides of a plane curvilinear triangle. The total curvature of an arc of a plane curve is equal to the external angle between the tangents at its extremities and must be carefully distinguished from the *average* curvature of the arc which is the quotient of its total curvature by its length. The angles of the curvilinear triangle *abc* (Fig. 2) are YaZ, ZbX, XcY. Their sum exceeds the sum of the angles of the *plane* triangle *abc* by $\angle\, Xbc + \angle\, Xcb + \angle\, Yca + \angle\, Yac + \angle\, Zab + \angle\, Zba$ which is equal to the sum of the external angles at X, Y, Z between the tangents. This result is cited on page 293 of Gibbs, I.

In conclusion it should be realised that c_1 and c_2 for a surface may have different signs so that the expression $c_1 + c_2$ may sometimes actually denote the *numerical* difference of the principal curvatures of a surface at a point. This occurs when the two principal sections produce curves which are convex to different parts. For example if one considers a mountain pass at its top lying between hills on each side, a vertical section of the surface of the mountain at the top of the pass made right across the traveller's path is concave upwards, while one made at right angles to this following the direction of traveller's path is concave downwards. The principal centres of curvature are on opposite sides of the surface in such a case and the principal radii of curvature are directed to opposite parts. The radii have opposite signs and the principal curvatures likewise. A surface is said to be "anticlastic" at such a point (as opposed to "synclastic," when the centres of curvatures are on one side and

c_1 and c_2 have the same sign). The surface of a saddle is another example. This will show the reader that a reference, as on page 318, to a surface for which $c_1 + c_2 = 0$ does not of necessity imply that the surface is plane. Quite a number of interesting investigations have been made by geometers on the family of surfaces which have the general property $c_1 + c_2 = 0$. An interesting example of a surface of "zero curvature" may be visualised thus. Imagine a string hanging from two points of support, in the curve known as a "catenary," and a horizontal line so far below it that the weight of a similar string stretching from the lowest point of the catenary to this line would be equal to the tension of the string at its lowest point. If one conceives the catenary curve to be rotated around this horizontal line, the resulting surface of revolution is an anticlastic surface such that its principal radii of curvature at each point are equal in magnitude but oppositely directed.

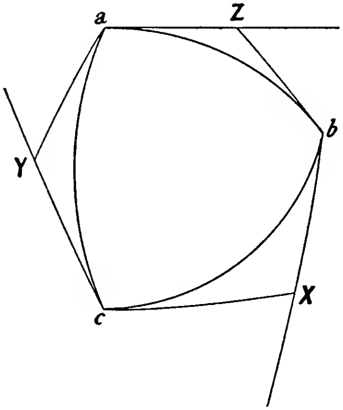

FIG. 2

*3. Quadric Surface.** The equation of a quadric surface, that is ellipsoid or hyperboloid, is

$$ax^2 + by^2 + cz^2 + 2\,fyz + 2\,gzx + 2\,hxy = k$$

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* To be read in conjunction with pp. 404, 410 of Article K of this Volume.

when the origin of the axes is at the centre of the surface. It can be proved that the equation of the plane which is tangent to the surface at the point x_1, y_1, z_1 on the surface is

$$(ax_1 + hy_1 + gz_1)\,x + (hx_1 + by_1 + fz_1)\,y$$
$$+ (gx_1 + fy_1 + cz_1)\,z = k.$$

Hence the direction-cosines of the normal to the surface at the point x_1, y_1, z_1 are proportional to the three expressions

$$ax_1 + hy_1 + gz_1, \quad hx_1 + by_1 + fz_1, \quad gx_1 + fy_1 + cz_1. \qquad (10)$$

Another result which is required concerns the changes in the coefficients in the equation of the surface if the axes of reference are transformed to another set of three orthogonal lines meeting at the centre. If the coordinates of a point are x, y, z referred to the old axes and x', y', z' referred to the new, the values of x, y, z can be worked out in terms of x', y', z' and the nine direction cosines of the new axes with reference to the old. On putting these values for x, y, z in the above expression, we obtain the equation of the quadric surface referred to the new axes as

$$a'x'^2 + b'y'^2 + c'z'^2 + 2\,f'y'z' + 2\,g'z'x' + 2\,h'x'y' = k,$$

where the values of a', b', c', f', g', h' can be obtained in terms of a, b, c, f, g, h and the nine direction cosines. The following three results can then be proved:

$$\left.\begin{aligned} a' + b' + c' &= a + b + c, \\ b'c' + c'a' + a'b' &- f'^2 - g'^2 - h'^2 \\ &= bc + ca + ab - f^2 - g^2 - h^2, \\ \begin{vmatrix} a' & h' & g' \\ h' & b' & f' \\ g' & f' & c' \end{vmatrix} &= \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix}. \end{aligned}\right\} \qquad (11)$$

The interested reader will find the proof in any standard text of analytical geometry.

A special case of considerable importance arises when the second set of axes of reference are the principal axes of the quadric surface. In that case it is known that f', g', h' are each zero and the equation of the surface has the form

$$a'x'^2 + b'y'^2 + c'z'^2 = k.$$

The results written above then become

$$\left.\begin{aligned} a' + b' + c' &= a + b + c, \\ b'c' + c'a' + a'b' &= bc + ca + ab - f^2 - g^2 - h^2, \\ a'b'c' &= \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix}. \end{aligned}\right\} \quad (12)$$

C

PAPERS I AND II AS ILLUSTRATED BY GIBBS' LECTURES ON THERMODYNAMICS

[*Gibbs, I, pp. 1–54*]

EDWIN B. WILSON

I. Introduction

As Papers I (pp. 1–32) and II (pp. 33–54) are properly characterised by H. A. Bumstead in his introductory biography (Gibbs, I, pp. xiv–xvi) as of importance not so much for any place they made for themselves in the literature as for the preparation and viewpoint they afforded the author as groundwork for his great memoir on the Equilibrium of Heterogeneous Substances, it will perhaps be most appropriate to illustrate them by an outline of Gibbs' course on thermodynamics as he gave it towards the end of his life. From such a sketch one may possibly infer what Gibbs himself considered important in the papers and what illustrations he himself thought it worth while to lay before his auditors. In this outline the notes of Mr. L. I. Hewes (now of the U. S. Bureau of Public Roads, San Francisco) who took the course in the academic year 1899–1900 will be followed.*

II. Outline of Gibbs' Lectures on Thermodynamics

Lecture I (*October 3, 1899*). The measurements in our subject fall into two sets, thermometry and calorimetry. Ordinary units of heat and scales of temperature. Constant pressure and constant volume thermometers. Gas thermometers with constant volume, pressure varying with the temperature, give best results. Clausius in his 1850 memoir brought order into the subject of thermodynamics—with references to Clausius in the original and in translations, and to Maxwell's Theory of Heat.

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* I took the course two years later in 1901–1902; my notes were lost, but unless my recollection is mistaken the course did not differ except by the inclusion, toward the end, of a few lectures on statistical mechanics and a more rapid advance in the earlier parts (see Note on p. 50).

Lecture II. Heat capacity (specific heat) at constant pressure and at constant volume. Work, $dW = pdv$. Relation between heat and work—first and second laws of thermodynamics. We take the second law first (Carnot's law). Carnot was a French army officer, son of a minister of war. He published his results at about 28 years of age. His father was also a mathematician and wrote on geometry and mechanics. (He was uncle of the late President Carnot.) Carnot's father named him Sadi after the Persian poet. Carnot's results meant an important question solved and interpreted.* The Carnot cycle or Carnot engine, a reversible cyclic process: Given a cylinder impervious to heat, except for the bottom which is a perfect conductor, filled with some medium (as air). Given a large hot and a large cold reservoir at assigned temperatures. Place the cylinder on the cold reservoir until the medium has taken the temperature of that. Carry out the following process. (1) Insulate the cylinder and compress the medium until the temperature has risen to that of the hot reservoir and then place the cylinder in contact with this reservoir. (2) Decompress the medium while the cylinder remains in contact with the reservoir thus absorbing heat and doing work at constant temperature. (3) Insulate and further decompress the medium until the temperature is lowered to that of the cold reservoir. (4) Place the cylinder in contact with the cold reservoir and compress to original volume. The result of the process is that some heat has been removed from the hot reservoir, some has been given to the cold reservoir, and some external work has been done.

Lecture III. Carnot's law: The same results are obtained with any medium when working between the same temperatures, or all reversible engines are exactly equivalent between the same temperatures. If you have two engines both using the same amount of heat, they must do the same amount of work. For if they do not, running one direct and the other reversed will do a net amount of work without the use of heat or any other change in the system from cycle to cycle, which would constitute a perpetual motion machine—a reductio ad absurdum. There is no perfectly reversible engine, but one can be approximated and for the purposes of reasoning one may be postulated.

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* The class notes of Mr. Hewes, carefully written up, show that Gibbs did not think it *infra dig.* to go into interesting bits of scientific history.

We assume that heat has to do with motion of the particles of a body. We have little doubt that matter consists of very small discontinuous particles and there is no reason they should not move. In regard to molecular motion forces are conservative; there are no frictional losses.

Lecture IV. Continuation of discussion of evidence of frictionless character of molecular motion. Count Rumford thought heat not a substance. Joule determined the mechanical equivalent of heat; $J = 772$ ft. pds. $W = JQ$. We may as well measure Q directly in mechanical units as $Q = W$. Carnot failed to establish the law $Q'' = Q' + W$, namely, that the difference between the heat received and the heat given up was (proportional to) the work done. Joule seems not to have been entirely clear about the conversion of heat into work. Clausius was the first to set these matters straight.

Lecture V. Discussion of meaning of first and second laws, and of various ways of stating them, by Tait, Clausius and Kelvin, illustrating each from considerations of the Carnot cycle. If Q'' be the heat taken in at one temperature and Q' that given out at the other and W the work done; and if q'', q', w be the similar quantities for another engine working between the same temperatures the quantities Q'', Q', W must be proportional to q'', q', w. For we could by multiplication (engines in parallel) make $Q' = mq'$. Now reversing one of the engines (or the set in parallel) the net heat taken or given to the cold reservoir would be nil and if the work were not also nil we should be obtaining work from heat at the single temperature of the hot reservoir which is contrary to Kelvin's statement of the second law. Hence $W = mw$ and since by the first law $Q'' - Q' = W$

and $q'' - q' = w$ we must have $Q'' = mq''$, which proves the theorem.*

Lecture VI. The first and second laws may be used to define a thermometric scale. For any two engines working between the same temperatures t_x and t_1 the heats received and given up satisfy the proportion

$$\frac{Q_x}{Q_1} = \frac{q_x}{q_1},$$

and hence these ratios may be taken as t_x/t_1. Thus

$$\frac{t_2}{t_1} = \frac{Q_2}{Q_1}, \qquad \frac{t_3}{t_1} = \frac{Q_3}{Q_1}, \qquad \text{and therefore } \frac{Q_3}{Q_2} = \frac{t_3}{t_2}.$$

This shows that t may be taken as proportional to Q or

$$\frac{Q_x}{t_x} = \frac{Q_y}{t_y}.$$

This is called the absolute thermodynamic scale and the only remaining freedom is to define the unit.

The first law is not confined to reversible cycles but the second law is. If we have two engines with
$Q'' - Q' = W$ (reversible or not) and $q'' - q' = W$ (reversible) and run the second backward so that no work is done, the net heat $Q'' - q''$ leaves the higher temperature and the equal amount $Q' - q'$ is received at the lower temperature. As heat cannot go without work from lower to higher temperature, $Q'' - q'' = Q' - q' \geqq 0$. Hence

$$\frac{Q'' - q''}{t''} \leqq \frac{Q' - q'}{t'},$$

the equality sign holding only when the numerators vanish, i.e., for the reversible case. But as $q''/q' = t''/t'$ we have

$$\frac{Q''}{t''} \leqq \frac{Q'}{t'} \text{ for any cycle.}$$

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* The slow development of the analytical part of the subject was noteworthy. It was Gibbs' intention that the student should thoroughly grasp the physical, historical, and logical background through ample discussion.

If in place of Q', the heat given up at t', we use $-Q'$ as the heat absorbed at t', the relation becomes

$$\frac{Q''}{t''} + \frac{Q'}{t'} \leqq 0.$$

With the understanding that Q_i represents the heat absorbed at the temperature t_i summation shows that

$$\sum \frac{Q_i}{t_i} \leqq 0 \quad \text{or} \quad \int \frac{dQ}{t} \leqq 0$$

is a statement of the second law, the equality sign holding for the reversible engine. The corresponding statement of the first law is $\Sigma\, Q_i = W$ or $\int dQ = W$.

Lecture VII (Oct. 23). The characteristic equation $f(p, v, t) = 0$. The pv diagram; isothermals and adiabatics. The work done in a circuit is the area of the circuit.

$$\int_0 dQ = \int_0 dW, \qquad \int_0 \frac{dQ}{t} \leqq 0.$$

If we define the energy as

$$\epsilon_1 - \epsilon_0 = \int_0^1 (dQ - dW),$$

ϵ is independent of the path since the circuit integral of $dQ - dW$ is zero. In like manner for reversible engines the quantity

$$\eta_1 - \eta_0 = \int_0^1 \frac{dQ}{t}$$

is independent of the path. It is called the entropy and like the energy is known except for an additive constant determinable when the arbitrary common origin of the paths is known. Then

$$dW = pdv, \qquad d\epsilon = dQ - dW, \qquad d\eta = dQ/t,$$
$$dQ = td\eta, \qquad d\epsilon = td\eta - pdv.$$

Of the seven quantities, five, namely, t, p, v, ϵ, η have particular values at any point of the diagram; the other two, Q, W have no certain values, being dependent on the path to that point.

Lecture VIII. Discussion of pv diagram. To get the heat Q_{AB} absorbed along a path from A to B draw the adiabatic from B and the isothermal from A intersecting in C and forming a curvilinear triangle ABC. Then

$$Q_{AB} = \text{area } ABC + (\eta_C - \eta_A)t_A.$$

The $t\eta$-diagram. Isometric and isopiestic lines. Carnot's cycle a simple rectangular figure. We may draw diagrams other than the pv-diagram or the $t\eta$-diagram for other purposes but they do not have the advantage of simple areal interpretations.*

The energy surface $\epsilon = f(\eta, v)$ as a function of entropy and volume.

$$\frac{d\epsilon}{d\eta} = t, \qquad \frac{d\epsilon}{dv} = -p.$$

Lecture IX. Review of fundamental concepts.

Lecture X. Mathematical transformations.

$$\text{Specific heats } C_p = \left(\frac{dQ}{dt}\right)_p, \qquad C_v = \left(\frac{dQ}{dt}\right)_v.$$

$$\text{Elasticities } E_\eta = -v\left(\frac{dp}{dv}\right)_\eta, \qquad E_t = -v\left(\frac{dp}{dv}\right)_t.$$

Proof of $C_p/C_v = E_\eta/E_t$ given first by calculus as usual and second geometrically by means of anharmonic ratios in the infinitesimal figure OV, OH, OT, OP formed by the intersection of a line $VHTP$ with the isometric, adiabatic, isothermal and isopiestic issuing from a point of the pv-diagram. The second proof is as follows:

$$\frac{C_P}{C_V} = \frac{\left(\dfrac{d\eta}{dt}\right)_P}{\left(\dfrac{d\eta}{dt}\right)_V} = \frac{\dfrac{\eta_P - \eta_O}{t_P - t_O}}{\dfrac{\eta_V - \eta_O}{t_V - t_O}} = \frac{\dfrac{\eta_P - \eta_H}{t_P - t_T}}{\dfrac{\eta_V - \eta_H}{t_V - t_T}} = \frac{\dfrac{PH}{PT}}{\dfrac{VH}{VT}}.$$

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* To this stage very little of the elaborate discussion of Paper I has been given. And no illustrative material. The lecture jumps right to Paper II. It may be particularly noted that the scale factor γ was not treated, nor the $v\eta$-diagram discussed at this stage in the course, though they were treated in Paper I.

The first and last steps depend merely on the infinitesimal characteristic of the figure and the intervening step on the definition of the iso-lines. Next, similarly,

$$\frac{E_\eta}{E_t} = \frac{\left(\dfrac{dp}{dv}\right)_\eta}{\left(\dfrac{dp}{dv}\right)_t} = \frac{\dfrac{p_H - p_O}{v_H - v_O}}{\dfrac{p_T - p_O}{v_T - v_O}} = \frac{\dfrac{p_H - p_P}{v_H - v_V}}{\dfrac{p_T - p_P}{v_T - v_V}} = \frac{\dfrac{HP}{HV}}{\dfrac{TP}{TV}}.$$

Lecture XI. About anharmonic ratios and in particular their independence of the choice of the secant line $VHTP$ inferable from the physical interpretation above.

Gases. $pv = f(t)$. Laws of Boyle and Charles, Mariotte and Gay-Lussac. $f(t) = at$. Practical measurement of C_p. Theoretical measurement of C_v. Measurements of E_η and E_t.

Lecture XII. Velocity of sound and its relation to the thermodynamic constants. Experiment with standing waves and lycopodium powder (Kundt's tube).

It is found that for a gas C_v and C_p/C_v are constant within close limits over a wide range of the pv diagram. The equation

$$d\epsilon = dQ - dW = dQ - pdv$$

reduces to $d\epsilon = dQ = C_v dt$ for constant volume and integrates into $\epsilon = C_v t + V(v)$ where the constant of integration is a function of the volume. Similarly for constant pressure we have $\epsilon = C_p t - pv + P(p)$. Comparing, and using $pv = at$,

$$V(v) - P(p) = (C_p - C_v - a)pv/a.$$

This indicates $C_p - C_v - a = 0$ and $V - P = 0$, so that if the zero of energy is taken at $t = 0$ we have $V = P = 0$ and the equations of the gases are

$$\epsilon = C_v t = C_p t - pv, \qquad a = C_p - C_v.$$

Lecture XIII. Review of fundamental equations. Discussion of differences between gas thermometer scale and absolute temperature defined by Carnot cycles. Further integration of fundamental equations. For adiabatic changes $d\epsilon = -pdv$ may be put in form

$$C_v \frac{d\epsilon}{\epsilon} = -a\frac{dv}{v}, \text{ or } \quad C_v \log \epsilon = -a \log v + H(\eta),$$

or for any change,

$$C_v \frac{d\epsilon}{\epsilon} = -a\frac{dv}{v} + \frac{dH}{d\eta}\,d\eta,$$

which, by the equations $\epsilon = C_v t$, $pv = at$, becomes

$$d\epsilon = -pdv + t\frac{dH}{d\eta}\,d\eta = dQ - dW = td\eta - dW.$$

Hence $dH/d\eta = 1$ and $H = \eta + \text{const}$; with the constant taken as $C_v \log C_v$ this makes*

$$C_v \log \frac{\epsilon}{C_v} = \eta - a \log v,$$

the equation between ϵ, η, v.

Lecture XIV. The differential $d\epsilon = td\eta - pdv$ gives

$$\left(\frac{d\epsilon}{d\eta}\right)_v = t, \qquad \left(\frac{d\epsilon}{dv}\right)_\eta = -p, \qquad \frac{d^2\epsilon}{d\eta dv} = \left(\frac{dt}{dv}\right)_\eta = -\left(\frac{dp}{d\eta}\right)_v.$$

Consider the function† $\psi = \epsilon - t\eta$ and $d\psi = -\eta dt - pdv$. Then

$$\left(\frac{d\psi}{dt}\right)_v = -\eta, \qquad \left(\frac{d\psi}{dv}\right) = -p, \qquad -\frac{d^2\psi}{dtdv} = \left(\frac{d\eta}{dv}\right)_t = \left(\frac{dp}{dt}\right)_v.$$

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[*] On comparison with the development, Gibbs, I, 12–13, formulas A to D, it will be seen that there are slight differences, but the method here given was followed by Gibbs in his course on thermodynamics in different years.

[†] I do not recall, and there is no evidence in the notes, that Gibbs gave names to the functions ψ, χ, ζ such as free energy, heat function, or thermodynamic potential. He appears not to have referred to the function $\Phi = \eta - (\epsilon + pv)/t = -\zeta/t$ which is widely used as a potential.

Consider the function $\chi = \epsilon + pv$ and $d\chi = td\eta + vdp$. Then

$$\left(\frac{d\chi}{d\eta}\right)_p = t, \qquad \left(\frac{d\chi}{dp}\right)_\eta = v, \qquad \frac{d^2\chi}{d\eta dp} = \left(\frac{dt}{dp}\right)_\eta = \left(\frac{dv}{d\eta}\right)_p.$$

Consider $\zeta = \epsilon - t\eta + pv$ and $d\zeta = -\eta dt + vdp$. Then

$$\left(\frac{d\zeta}{dt}\right)_p = -\eta, \qquad \left(\frac{d\zeta}{dp}\right)_t = v, \qquad \frac{d^2\zeta}{dtdp} = -\left(\frac{d\eta}{dp}\right)_t = \left(\frac{dv}{dt}\right)_p.$$

The four Maxwell relations. For perfect gases

$$\eta = C_v \log p + (C_v + a) \log v - C_v \log a = C_v \log t + a \log v,$$

$$\psi = C_v t - C_v t \log t - at \log v,$$

with similar expressions in ζ and χ. The fundamental forms imply that ϵ is a function of η, v; that ψ is a function of t, v; that χ is a function of η, p; and that ζ is a function of t, p.

Lecture XV. Avogadro's law. This differs from the laws thus far considered in that it relates to the invisible, molecular, properties of a gas instead of to the observable properties. The equation of a gas becomes $pv = A(m/M)t$ where m is the mass of the gas and M is the molecular weight.

Lecture XVI. A gas mixture has the equation

$$pv = \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \cdots\cdot + \frac{m_n}{M_n}\right) At.$$

The translational kinetic energy of the molecules is proportional to the pressure and therefore to the temperature.

Lecture XVII. The geometric interpretation of p and t on the thermodynamic surface $\epsilon(\eta, v)$. The use of the surface is to aid in thermodynamic investigations. The equation of the surface is known for a perfect gas, but the idea of it is equally applicable to any substance which need not be in a homogeneous state. Discussion of a substance in a liquid and vapor phase; rulings on the surface; the pv-diagram.

Lecture XVIII. The solid-liquid and solid-vapor lines; the "triple-point" and the triply tangent plane. The relation

$$\frac{dp}{dt} = \frac{Q}{(v_V - v_L)t}$$

for the invariant system consisting of liquid and vapor.

Lecture XIX. Integrate $d\epsilon = td\eta - pdv$ from liquid to vapor phase, t and p being constant.

$$\epsilon_V - \epsilon_L = t(\eta_V - \eta_L) - p(v_V - v_L)$$

or

$$\zeta_V = \epsilon_V - t\eta_V + pv_V = \epsilon_L - t\eta_L + pv_L = \zeta_L.$$

The function ζ has the same value. The interpretation of ζ as the intercept of the tangent plane on the ϵ-axis. The equation

$$d\zeta_V = d\zeta_L \quad \text{gives} \quad \frac{dp}{dt} = \frac{\eta_V - \eta_L}{v_V - v_L} = \frac{Q}{(v_V - v_L)t}.$$

The discontinuity of dp/dt at the freezing point. Discussion of the physical meaning of the Maxwell relations.

Lecture XX.[*] In the pv-diagram the isothermals in the vapor state start from large values of v approximately like the hyperbolas $pv = at$; as v decreases their form is modified somewhat because when the vapor becomes dense the relation $pv = at$ is somewhat inexact If the vapor starts to condense for values $p = p', v = v'$ the isothermal becomes a straight line $p = p'$ and so remains until condensation is completed at $p = p' = p''$ and $v = v'' < v'$. From this point as v decreases the isothermal rises rapidly because a liquid is compressed only with rapidly increasing pressure. The locus of the points (p', v') and

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[*] To this point the lecturer had been following his two Papers I and II (Vol. I, pp. 1–54) with numerous omissions, with very few modifications, and with considerable elaboration of the physical principles and facts underlying the subject. From here on he goes into a very considerable development, which though perfectly natural and now found in other books, is not found in his writings. It seems that these applications of his own may have so great an interest as to justify following them in considerable detail in the order of his thought.

(p'', v'') forms a curve which we call the critical locus. If the temperature is high enough there will be no condensation. It has been seen that ζ is constant for the rectilinear portion of the isothermal including its extremities which lie upon the critical locus.

For any path connecting these two limiting points (p', v') and (p'', v'') with $p' = p''$ upon the isothermal t the total change of ζ must be nil. Now

$$\epsilon'' - \epsilon' = \int d\epsilon = \int dQ - \int p dv,$$

$$\eta'' - \eta' = \int dQ/t,$$

$$p''v'' - p'v' = \int (p dv + v dp).$$

If the second equation be multiplied by $-t' = -t''$ and the three be added

$$(\epsilon'' - t''\eta'' + p''v'') - (\epsilon' - t'\eta' + p'v')$$
$$= \int dQ - t' \int dQ/t + \int v dp = 0.$$

Hence for any path joining the two points

$$\int \frac{t - t'}{t} dQ + \int v dp = 0.$$

In particular if the path be taken as a line $v = v'$ rising above the critical point to $p = p'''$, a line $p = p'''$ to the value $v = v''$, and finally the line $v = v''$ to $p = p''$ (the three lines forming three sides of a rectangle of which the straight portion of the isothermal is the base), the value of $\int v dp$ is $(v'' - v')(p' - p''')$ and thus for this path

$$\int \frac{t - t'}{t} dQ + (v'' - v')(p' - p''') = 0.$$

We have seen that $pv = at$ is a law satisfied within wide limits. The law

$$p = \frac{\alpha}{v^2} + \frac{at}{v - b},$$

proposed by van der Waals, reduces essentially to $pv = at$ when v is large and is found to be an improvement on that equation for smaller values of v. For large values of t the isothermals in the pv-diagram are concave upwards throughout their course from $v = \infty$ to $v = b$ where they become infinite; for small values of t the concavity changes and indeed the curves have a maximum and minimum. An isothermal of this type may have some degree of realization; for the phenomena of the super-cooled vapor in which condensation does not start and of super-heated liquid in which vaporization does not start are known, and indicate that under suitable conditions the isothermals of the vapor state may cross the critical line as the volume is reduced and the isothermal of the liquid state may also cross that line when the volume increases. The part of the isothermal of van der Waals which lies between the minimum and maximum and for which dp/dv is positive cannot be expected to be realized, as a positive value of dp/dv represents a mechanically unstable condition. If nonetheless one writes $d\zeta = -\eta dt + vdp$ and integrates along an isothermal one has $\zeta'' - \zeta' = \int vdp$ and as for coexistent states $\zeta'' - \zeta' = 0$, one must have for such states $\int vdp = 0$. This means that from any van der Waals isothermal the line $p = p' = p''$, which is the physical isothermal corresponding to coexistent states for the same temperature, must cut off equal areas, one below the line and the other above it.

If the series of isothermals be drawn there are three interesting loci, the critical locus which gives the limiting conditions of coexistence of vapor and liquid phases, the locus of maxima and minima, and the locus of the point at which the rising (unrealizable) part of the isothermal cuts the line $p = p' = p''$.

Lecture XXI. The word "unstable" is used in thermodynamics in not quite the same sense as in mechanics. If we have a supersaturated solution crystallization may not start; the substance may be stable within limits to certain variations, but will start to crystallize rapidly if a minute crystal be introduced, i.e., the solution may be unstable to the introduction of the crystal phase. So in superheated water, there may be stability with respect to various processes, but not with respect to the introduction of a bubble of steam.

Entropy has been defined for a body considered homogeneous; the restriction may be removed. There would be no difficulty with respect to coexistent homogeneous phases such as a substance part liquid and part vapor which has been under discussion; we should add the entropies as well as the volumes and energies of the two parts. It is, however, necessary to proceed with some caution because entropy and energy have arbitrary origins and it is essential that the entropy and energy in one phase should be consistent with those in any other phase into which the substance may go or from which it may come. Suppose we have a substance in various phases, and not necessarily all in one working unit. Suppose the substance receives amounts $Q_1, Q_2, \ldots$ of heat at temperature $t_1, t_2, \ldots$, negative values of Q meaning that heat is returned to the reservoir. Also a certain amount of work is done by the substance or on it. The number of temperatures $t_1, t_2, \ldots$ of the reservoirs from which the substance receives heat may be infinite. Let the substance work on a cyclic process or on cyclic processes which may or may not be reversible. With this entire system we combine a perfect (reversible) thermodynamic engine or a number of such engines to take the quantities of heat $Q_2, \ldots$ all to a reservoir of the given temperature t_1. The quantities may be schematized as follows:

Reservoir temperatures	t_1,	t_2,	t_3,	$t_4, \ldots$
Heat absorbed by system	Q_1,	Q_2,	Q_3,	$Q_4, \ldots$
Heat used by engines		$-Q_2$,	$-Q_3$,	$-Q_4, \ldots$
Heat yielded by engines		$\frac{t_1}{t_2} Q_2$,	$\frac{t_1}{t_3} Q_3$,	$\frac{t_1}{t_4} Q_4, \ldots$
Work done by engines		$\frac{t_1 - t_2}{t_2} Q_2$,	$\frac{t_1 - t_3}{t_3} Q_3$,	$\frac{t_1 - t_4}{t_4} Q_4, \ldots$
Work done by system	Q_1,	$+Q_2$,	$+Q_3$,	$+Q_4, \ldots$

As the whole complex consisting of the system and the engines is cyclic, the total work done, which is

$$Q_1 + \frac{t_1}{t_2} Q_2 + \frac{t_1}{t_3} Q_3 + \frac{t_1}{t_4} Q_4 + \dots,$$

must be negative or zero as we cannot obtain work by a cyclic process without creating a perpetual motion machine. Hence dividing by t_1, which is positive, we have

$$\frac{Q_1}{t_1} + \frac{Q_2}{t_2} + \frac{Q_3}{t_3} + \frac{Q_4}{t_4} + \dots = \Sigma \frac{Q}{t} \leqq 0, \quad \text{or} \quad \int \frac{dQ}{t} \leqq 0,$$

the equality sign holding only when the system is reversible.

Now let s be any state of reference of the body for which we take $\eta = 0$; then any states 1 and 2 which can be reached from s by a reversible process will have the entropies

$$\eta_1 = \int_s^1 \frac{dQ}{t}, \qquad \eta_2 = \int_s^2 \frac{dQ}{t},$$

and the difference between the entropies will be

$$\eta_2 - \eta_1 = \int_1^2 \frac{dQ}{t},$$

where there is obviously one reversible way to go from 1 to 2, namely, that via s reversing the path from 1 to s above and following the path from s to 2. For example, if we have a saturated solution in equilibrium with some crystals, the application of heat will dissolve the crystals maintaining a saturated solution until such point as the crystals are all dissolved and the further application of heat will render the solution unsaturated. Next, if heat be withdrawn the solution will become saturated and then possibly somewhat supersaturated rather than crystallizing. This process is reversible; if the solution were supersaturated application of heat would render it unsaturated. The transition from the state of saturation in the presence of crystals to an unsaturated state through the application of heat is however not necessarily reversible because of the phenomenon of supersaturation; but there is generally some way to induce crystallization so that we can consider that the state of saturation in the presence of crystals may be reached reversibly. If this is the case it is easy enough to define the difference in entropy between a state of supersaturation and the state of saturation in the presence of crystals.

Consider next a process which goes on within a wholly isolated system doing no work and receiving no heat. If that system can exist in two states 1 and 2 such that the path from 1 to 2 is irreversible but the path from 2 to 1 is reversible we can represent the difference in entropy at 2 and at 1 as $\eta_2 - \eta_1$. Then

$$\underset{\text{irrev.}}{\int_1^2 \frac{dQ}{t}} + \underset{\text{rev.}}{\int_2^1 \frac{dQ}{t}} \leqq 0 \quad \text{and} \quad \underset{\text{irrev.}}{\int_1^2 \frac{dQ}{t}} \leqq \eta_2 - \eta_1.$$

But if the irreversible process goes on entirely within the system there will be no heat dQ absorbed by the system, $dQ = 0$, and hence

$$0 \leqq \eta_2 - \eta_1 \quad \text{or} \quad \eta_2 \geqq \eta_1.$$

Hence if an isolated system changes from state 1 to state 2, the entropy in state 2 must exceed that in state 1 (except when the change is reversible, when $\eta_2 = \eta_1$). It is assumed that there is some way to reach both states 1 and 2 reversibly from a third state. Take the case of the supersaturated solution. This may go over of itself into the state of a saturated solution with crystals. We have seen that we can reach the supersaturated states reversibly (i.e., we can reach any attainable degree of supersaturation reversibly). We can reach the state of saturation in the presence of crystals by merely placing the saturated solution and the crystals in juxtaposition. We have thus the possibility of defining the entropy η_2 of the mixture of saturated solution and crystals and the entropy η_1 of the supersaturated solution. The difference $\eta_2 - \eta_1$ will be positive. It is assumed that the mixture of saturated solution and of crystals in all its characteristics is that which would result from the spontaneous crystallization of the supersaturated solution in complete isolation.

The thermodynamic surface $\epsilon(\eta, v)$ represents the various states of a substance. There is a plane tangent to the surface at three points representing the three phase possibilities, solid, liquid, vapor. If the energy, entropy and volume of unit masses of the substance in contact with each other in solid, liquid and vapor state are ϵ_S, η_S, v_S; ϵ_L, η_L, v_L; ϵ_V, η_V, v_V, respectively, then the energy, entropy and volume of a unit mass of which m_S is solid, m_L is liquid, m_V is vapor are

$$\epsilon = m_S\epsilon_S + m_L\epsilon_L + m_V\epsilon_V,$$

$$\eta = m_S\eta_S + m_L\eta_L + m_V\eta_V,$$

$$v = m_Sv_S + m_Lv_L + m_Vv_V,$$

with $m_S + m_L + m_V = 1$. There are developable surfaces corresponding to the equilibrium between liquid and vapor, between solid and liquid, and between solid and vapor. There are curved surfaces to represent the pure phases vapor or liquid or solid. The thermodynamic surface is constituted of all these parts. In addition to this there may be parts of the surface which may be actually realized to some extent corresponding to supersaturation when the liquid fails to crystallize and superheating when the liquid fails to vaporize. Such parts of the surface must lie inside the surface as viewed from the positive end of the entropy axis because they must represent states in which the entropy is less than it is in states into which the substance may spontaneously go.

Let A and B be any two points of the thermodynamic surface which represents the entirely stable states. The segment AB must lie within (or on) the surface as viewed from the positive entropy axis. For consider any point P on AB and instead of the unit of substance for which the surface is given consider a mixture of AP/AB units of the substance in the state represented by A with PB/AB units of substance in the states represented by B. The energy and volume and entropy of the mixture are

$$\epsilon_P = \frac{AP}{AB}\epsilon_B + \frac{PB}{AB}\epsilon_A,$$

$$v_P = \frac{AP}{AB} v_B + \frac{PB}{AB} v_A,$$

$$\eta_P = \frac{AP}{AB} \eta_B + \frac{PB}{AB} \eta_A.$$

Shut up in the volume v and isolated, changes will go on in the mixture which while unable to change ϵ or v will increase η. Thus the unit of the substance will come to equilibrium at a point on the thermodynamic surface $\epsilon = \epsilon_P$, $v = v_P$, $\eta \geqq \eta_P$. As the proof holds for any point P no point between A and B can lie in the surface unless they all do. It follows that if a tangent plane is drawn to the surface at any point which represents an entirely stable state of the body no point of the surface can lie on that side of the plane for which entropy is greater. Physically, in any change that would increase η but involves the formation of a state widely different (such as a new phase) there is a certain reluctance* to take the step and this phenomenon gives rise to states which for some variations behave as stable states but for others give indications of not being entirely stable.*

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* Lewis and Randall in their *Thermodynamics, and the Free Energy of Chemical Substances*, McGraw-Hill (1923), say, on p. 17: "In the work of Gibbs and some other writers upon thermodynamics, some processes are supposed to be of infinite slowness, but this view of the existence of a so-called "passive resistance" is apparently not supported by experimental evidence . . . ." The term "passive resistance" is apparently not used by Gibbs in Papers I and II; but that he would have regarded the reluctance to change exhibited in the phenomena of supercooling, superheating and supersaturating as due to such resistances is rendered likely by his definitions and illustrations when he first introduces the term, namely, in Paper III (Gibbs, I, p. 58) where he writes: "In order to apply to any system the criteria of equilibrium which have been given, a knowledge is requisite of its passive forces or resistances to change, in so far, at least, as they are capable of *preventing* change. (Those passive forces which only retard change, like viscosity, need not be considered.) . . . As examples, we may instance the passive force of friction which prevents sliding when two surfaces of solids are pressed together, . . . , that resistance to change which sometimes prevents either of two forms of the same substance (simple or compound), which are capable of existing, from passing into the other. . . . " It certainly does not appear from this phraseology that Gibbs was supposing the processes which he associated with the term passive resistance to be of infinite slowness; indeed his underlining of the word *preventing* and his

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excepting those passive forces which only retarded change seem clearly to indicate that there was a state of no process whatsoever associated with the passive resistances rather than one of very slow process. And again in the discussion of Certain Points Relating to the Molecular Constitution of Bodies (Gibbs, I, pp. 138-144) he seems to be drawing a possible logical distinction between passive resistances which prevent change and those which only slow it down, though they may slow it down very greatly. He certainly does seem to postulate that there may be real states of equilibrium which are not states of dissipated energy and which do not even with infinite slowness go over into such states. Lewis and Randall would appear to postulate that there are in reality no such states, that only states of dissipated energy are states of equilibrium. They may be entirely right without Gibbs being in any way wrong. It is important to have the solutions for both ideal cases—that in which the change is absolutely prevented and that in which it is completely consumated. A case in practice may well be intermediate between the two so that both solutions might be inapplicable. Gibbs speaks as though hydrogen and oxygen placed together at room temperature would never unite to form water vapor; while Lewis and Randall expect them to unite (almost completely, though slowly) according to their equation (22), p. 485, viz., $H_2 + \frac{1}{2}O_2 = H_2O(g)$; $\Delta F^\circ_{298} = -54507$, and so, too, we may presume that if hydrogen were shut up by itself they would expect it to go over into helium. There is, of course, no practical difference between the two postulates when the reaction is slow enough, but it would seem that Gibbs' form would be at least as convenient practically as that of Lewis and Randall.

* The logical difference between stability and slowness in attaining the stable state must be kept in mind. Thus a liquid in the presence of its vapor may be very slow in evaporating to the point where the vapor is saturated and the equilibrium is established. Things do not dry immediately simply because there is not equilibrium between their state of wetness or dryness and the humidity in the atmosphere. In thermodynamics time is disregarded, the processes are permitted to take place infinitely slowly. Indeed finite velocities may introduce irreversibility. For example in the simple Carnot cycle in the decompression stage 2 (Lecture II) it is specified that the decompression is isothermal, which means that it is slow enough so that the medium remains at the temperature of the reservoir. If the medium were a perfect gas $pv = at$, the work would be $W = \int pdv = at \log (v_2/v_1)$. But if the decompression be fast enough the medium would expand practically adiabatically (and

Lecture XXII (December 18, 1899). A detailed discussion of the characteristics of the thermodynamic surface with respect to increasing entropy.*

Lecture XXIII (January 11, 1900). The surface lies on the negative entropy side of any tangent plane. If the surface in the immediate vicinity of the point of tangency lies on the negative entropy side of the plane, the substance is in a stable state for infinitesimal variations from the state represented by the point of tangency. In like manner as an isolated system tends to a state of minimum energy it follows that if the surface lies upon that side of the tangent plane upon which energy increases the state represented by the point of tangency will be one of stable equilibrium; if at a considerable distance from this point the plane again cuts the surface we have a kind of instability (the state is not entirely stable) but there is still stability for small variations.

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then heat up from the reservoir). The work would be less, say w. By the time the medium had absorbed the heat from the reservoir its energy would however be the same. For the two processes we have therefore $Q - W = q - w$ or $Q - q = W - w > 0$ or $Q > q$. When the heat Q is transferred from the reservoir to the medium isothermally at temperature t, the medium gains entropy to the amount Q/t and the reservoir loses the same amount of entropy. In the adiabatic decompression and subsequent heating the medium gains the same amount of entropy Q/t but the reservoir loses only q/t so that the system consisting of reservoir and medium gains the amount $(Q - q)/t$ of entropy. To put this in another light suppose there are two like cylinders one in condition v_1, t which expands adiabatically to state v_2, t and then heats up as above and the other in state v_2, t which is compressed isothermally in contact with the reservoir to (v_1, t) as in stage (4) of the Carnot cycle. The operation of the two will result in work $W - w$ being done on the media. In the final condition the two cylinders have only interchanged states. The reservoir has gained the heat $Q - q$ equivalent to the work done and the system consisting of the two cylinders and medium will have gained the entropy $(Q - q)/t$ representing the irreversibility in the process.

* This was essentially a review and illustration of the close of the previous lecture, consideration being also given to the kind of isothermals encountered in van der Waals' equation. It does not seem worth while to follow this detail here, though it was helpful to the class in gaining a better appreciation of the subject matter. The long Christmas vacation intervened at this point in the course.

Conditions for stability. Let $z = f(x, y)$.

$$z = z_0 + \frac{dz}{dx}\Delta x + \frac{dz}{dy}\Delta y$$

$$+ \tfrac{1}{2}\left(\frac{d^2z}{dx^2}\Delta x^2 + 2\frac{d^2z}{dxdy}\Delta x\Delta y + \frac{d^2z}{dy^2}\Delta y^2\right) + \ldots.$$

Tangent plane

$$z_p = z_0 + \frac{dz}{dx}\Delta x + \frac{dz}{dy}\Delta y,$$

$$z - z_p = \tfrac{1}{2}\left(\frac{d^2z}{dx^2}\Delta x^2 + 2\frac{d^2z}{dxdy}\Delta x\cdot\Delta y + \frac{d^2z}{dy^2}\Delta y^2\right) + \ldots.$$

Neglecting higher powers, the condition that $z > z_p$, except for $\Delta x = \Delta y = 0$, is first

$$\frac{d^2z}{dx^2} > 0 \quad \text{and} \quad \frac{d^2z}{dy^2} > 0,$$

and then by completing the square also

$$\frac{d^2z}{dx^2}\frac{d^2z}{dy^2} - \left(\frac{d^2z}{dxdy}\right)^2 > 0.$$

For the limit of stability this last condition is zero. Replace z by ϵ and x, y by η, v and remembering $d\epsilon = td\eta - pdv$ the conditions are

$$\frac{d^2\epsilon}{dv^2} = -\left(\frac{dp}{dv}\right)_\eta > 0, \qquad \frac{d^2\epsilon}{d\eta^2} = \left(\frac{dt}{d\eta}\right)_v > 0,$$

$$\frac{d^2\epsilon}{dv^2}\frac{d^2\epsilon}{d\eta^2} - \left(\frac{d^2\epsilon}{dvd\eta}\right)^2 = -\left(\frac{dp}{dv}\right)_\eta\left(\frac{dt}{d\eta}\right)_v - \left(\frac{dp}{d\eta}\right)_v^2 > 0.$$

The first condition means that when the change is adiabatic p must decrease as v increases, and the second means that at constant volume the temperature must rise if heat is supplied. The third condition may be transformed. Note first that

$$\frac{d^2\epsilon}{d\eta dv} = -\left(\frac{dp}{d\eta}\right)_v = \left(\frac{dt}{dv}\right)_\eta.$$

Now for constant volume p generally increases if heat is supplied, and under adiabatic conditions the temperature generally rises under compression; hence generally this second derivative is negative. But for water under the temperature of maximum density the results are reversed and the derivative is positive. Next

$$dp = -d\left(\frac{d\epsilon}{dv}\right)_\eta = -\frac{d^2\epsilon}{dvd\eta}d\eta - \frac{d^2\epsilon}{dv^2}dv = -Bd\eta - Adv,$$

$$dt = d\left(\frac{d\epsilon}{d\eta}\right)_v = \frac{d^2\epsilon}{d\eta^2}d\eta + \frac{d^2\epsilon}{dvd\eta}dv = Cd\eta + Bdv.$$

Solve for $d\eta$ and dv; then

$$\left(\frac{dp}{dv}\right)_t = -\frac{AC - B^2}{C}, \qquad \left(\frac{dt}{d\eta}\right)_p = \frac{AC - B^2}{A},$$

$$\left(\frac{dp}{d\eta}\right)_t = \frac{AC - B^2}{B}, \qquad \left(\frac{dt}{dv}\right)_p = -\frac{AC - B^2}{B}.$$

Now as $C > 0$, $AC - B^2 > 0$, this means that on an isothermal p must decrease with increasing v. So, too, at constant pressure the temperature must increase with a supply of heat. In the general case where $B < 0$, supplying heat and maintaining a constant temperature must decrease the pressure, or at constant pressure the temperature must increase with the volume. Note that equating the last two expressions and inverting the derivatives yields the Maxwell relation obtained from the function ζ.

Lecture XXIV. Discussion of van der Waals' equation.*

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* The development may not seem logical and was probably adopted for pedagogic reasons. As early as Lecture XVII the pv-diagram for vapor, liquid, and vapor-liquid phases was introduced, leading from physical reasoning to the definition of critical locus and the conception of that sort of stability or instability which is represented by the supercooled vapor or superheated liquid. On this basis in Lectures XVIII–XIX properties of the thermodynamic surface were discussed. In Lecture XX the equation of van der Waals was cited as affording possible conceptual though largely unrealizable isothermals through the critical region, and this type of isothermal was kept to the fore, in parallel with

Here

$$p = -\frac{\alpha}{v^2} + \frac{Rt}{v - b}, \tag{1}$$

$$\left(\frac{dp}{dv}\right)_t = \frac{2\alpha}{v^3} - \frac{Rt}{(v - b)^2} = 0 \tag{2}$$

at the limit of stability. Eliminating t, the locus in the pv plane is*

$$p = \frac{\alpha}{v^2} - \frac{2\alpha b}{v^3}. \tag{3}$$

We have also the equation

$$\left(\frac{d^2p}{dv^2}\right)_t = -\frac{6\alpha}{v^4} + \frac{2Rt}{(v - b)^3} = 0 \tag{4}$$

to represent the inflections of the isothermals. Equations (1), (2), (4) have a common solution, which must be also a solution of (3), and this is the critical point. If (1) be regarded as a cubic in v the critical point is that for which the cubic has three equal roots. For this point

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the actual physical isothermal representing complete equilibrium, in the detailed discussion of the thermodynamic surface including the questions of stability (whether entire or limited) in Lectures XX–XXIII. This general discussion completed, the lecturer returns to a considerable development and illustration with the aid of the equation of van der Waals.

* The limit of stability is defined by $(dp/dv)_t = 0$, i.e., when $AC - B^2 = 0$. It may be observed that by this definition there may lie within the limit of stability states with negative values of p, i.e., with tensions instead of pressures. From (3) we have $v = 2b$ when $p = 0$. Then $Rbt/\alpha = 1/4$. In terms of the critical values $v/v_c = 2/3$, $t/t_c = 27/32$. Thus for temperatures below $27t_c/32 = .844t_c$ the van der Waals' isothermal dips down to negative values of p. Indeed as v decreases toward b, p in (3) decreases toward $-\alpha/b^2 = -27p_c$, and t toward zero. Although all negative values of p represent instability in vapor phases, we do know that under careful experimental conditions liquids can be made to support very considerable tensions without going over into the vapor phase, thus parts of these isothermals for negative p can be realized qualitatively even if the quantitative relations are quite inadequately represented by (1).

$$v_c = 3b, \qquad p_c = \frac{1}{27}\frac{\alpha}{b^2}, \qquad t_c = \frac{8\alpha}{27\,Rb}, \tag{5}$$

and

$$b = \frac{v_c}{3}, \qquad \alpha = 3\,p_c v_c^2, \qquad R = \frac{8}{3}\frac{p_c v_c}{t_c}. \tag{6}$$

There is no great difficulty in determining p_c, t_c from observation. Sketch of possible methods. The determination of v_c is more difficult because infinitesimal changes in v near v_c produce changes of p, t from p_c and t_c which are infinitesimals of higher order and hence slight changes in p and t from p_c and t_c produce large variations in v from v_c,—as may be seen geometrically from the shape of the isothermals in the vicinity of the critical point. However, we may determine v_c by the known value of R.

Lecture XXV. Discussion of the accuracy with which van der Waals' equation represents the physical facts. The critical locus may be obtained from the condition that $\int p dv$ along the isothermal from one of its intersections (p, v_1) with the critical locus to the other (p, v_2) must be equal to $p(v_2 - v_1)$ by the areal of property previously proved. Hence

$$p(v_2 - v_1) - \frac{\alpha}{v_2} + \frac{\alpha}{v_1} + Rt \log \frac{v_1 - b}{v_2 - b} = 0. \tag{7}$$

Equation (1) holds for p, v_1, t and for p, v_2, t. Eliminate p, t. Then

$$\frac{v_2 + v_1}{v_2 - v_1} \log \frac{v_1 - b}{v_2 - b} + \frac{v_1}{v_1 - b} + \frac{v_2}{v_2 - b} = 0.$$

Let

$$V_1 = \frac{v_1 - b}{b}, \qquad V_2 = \frac{v_2 - b}{b}.$$

Then with $P = V_1/V_2$ we have

$$\frac{1}{V_2} = \frac{2 - \dfrac{P+1}{P-1}\log P}{\dfrac{2\log P}{P-1} - \dfrac{1}{P} - 1}, \qquad V_1 = PV_2.$$

At the critical point $V_1 = V_2$, $\log P = 0$. We may take $P \leqq 1$. Furthermore

$$\frac{bRt}{\alpha} = \frac{(V_1 + V_2 + 2)\, V_1 V_2}{(V_1 + 1)^2\, (V_2 + 1)^2},$$

$$\frac{b^2 p}{\alpha} = \frac{V_1 V_2 - 1}{(V_1 + 1)^2\, (V_2 + 1)^2},$$

and*

$$V_3 = \frac{Rt}{bpV_1V_2} = \frac{V_1 + V_2 + 2}{V_1 V_2 - 1}.$$

The critical locus may therefore be plotted from the following computation form

P	V_2	V_1	bRt/α	b^2p/α	V_3
1.0	2.0	2.0	.296	.0370	2.00
.9	2.11	1.90	.296	.0370	2.00
.8	2.24	1.79	.296	.0368	2.00
.7	2.40	1.68	.295	.0365	2.01
.6	2.60	1.56	.294	.0360	2.02
.5	2.86	1.43	.292	.0351	2.03
.4	3.23	1.29	.290	.0338	2.06
.3	3.79	1.14	.285	.0316	2.10
.2	4.77	.95	.277	.0279	2.17
.1	7.23	.72	.259	.0210	2.36
.05	11.21	.56	.238	.0146	2.61
.02	20.76	.42	.211	.0080	3.04
.01	33.98	.34	.191	.0048	3.44
.005	56.79	.28	.173	.0027	3.91
.002	115.24	.23	.153	.0012	4.60
.001	200.58	.20	.139	.0007	5.17

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* The intermediate value V_3 where the ascending branch of the isothermal cuts the horizontal is obtainable from

$$b^3 V_1 V_2 V_3 = v_1 v_2 v_3 - b(v_1 v_2 + v_1 v_3 + v_2 v_3) + b^2(v_1 + v_2 + v_3) - b^3$$

which may be evaluated at once from van der Waals' equation.

One may plot in the same diagram the isothermals from

$$\frac{b^2 p}{\alpha} = \frac{Rbt/\alpha}{V} - \frac{1}{(V+1)^2},$$

and the locus of the limit of stability from

$$\frac{b^2 p}{\alpha} = \frac{2\,V}{(V+1)^3} - \frac{1}{(V+1)^2}.$$

The table is good for any substance satisfying van der Waals' equation.

Lecture XXVI. If $\psi = \epsilon - t\eta$, $d\psi = -\eta dt - p dv$, and

$$-p = \left(\frac{d\psi}{dv}\right)_t = \left(\frac{\alpha}{v^2} - \frac{Rt}{v-b}\right)_t$$

may be integrated to find

$$\psi = -\frac{\alpha}{v} - Rt \log (v - b) + \Phi(t), \tag{8}$$

$$\eta = -\left(\frac{d\psi}{dt}\right)_v = R \log (v-b) - \Phi'(t), \tag{9}$$

$$\epsilon = -\frac{\alpha}{v} + \Phi(t) - t\,\Phi'(t), \tag{10}$$

$$C_v = \left(\frac{d\epsilon}{dt}\right)_v = -t\,\Phi''(t). \tag{11}$$

If the volume is very great the specific heat for constant volume is ordinarily constant, say c. Then $-\Phi'(t) = c \log t +$ const., and the constant may be taken as zero without loss of generality. Hence

$$\Phi(t) = ct - ct \log t, \tag{12}$$

and for a substance satisfying van der Waals' equation we have

$$\psi = -\frac{\alpha}{v} - Rt \log (v-b) + ct - ct \log t, \tag{13}$$

$$\eta = R \log (v-b) + c \log t, \tag{14}$$

$$\epsilon = -\frac{\alpha}{v} + ct. \tag{15}$$

The last two equations consist of sums of a function of v and a function of t. The thermodynamic surface is

$$\eta = R \log (v - b) + c \log \frac{\epsilon + a/v}{c} \tag{16}$$

or

$$\epsilon = -\frac{\alpha}{v} + c\frac{e^{\eta/c}}{(v - b)^{R/c}}. \tag{17}$$

This surface is that which corresponds to following the substance through its partly stable and its unstable states which correspond to the parts of the isothermals within the critical locus; it is, therefore, not precisely the thermodynamic surface discussed in Lecture XXI.

We may obtain $\zeta = \epsilon - t\eta + pv$ as

$$\zeta = -\frac{\alpha}{v} - Rt \log (v - b) + ct - ct \log t + pv. \tag{18}$$

This is not the desired form, which should involve p and t, but the elimination of v would require the solution of a cubic equation. The condition for corresponding states is $\zeta_2 = \zeta_1$ and this reduces to (7) which was obtained above.

Corresponding states. By introducing the values of α, b, R in terms of p_c, v_c, t_c into the equation and using

$$P = p/p_c, \qquad V = v/v_c, \qquad T = t/t_c,$$

van der Waals' equation takes the form

$$P = -\frac{3}{V^2} + \frac{\frac{8}{3}T}{V - \frac{1}{3}} \tag{19}$$

which is of the same form for all substances, but with pressure, volume and temperature expressed as multiples of the (different) critical values for the (different) substances.

Lecture XXVII. The tangent plane to the thermodynamic surface is

$$\epsilon - \epsilon_o = t(\eta - \eta_o) - p(v - v_o).$$

The slopes of the plane are t in the $\epsilon\eta$ plane or planes parallel thereto and $-p$ in the ϵv plane or any parallel plane. Further

$$-dp = Adv + Bd\eta, \qquad dt = Bdv + Cd\eta,$$

with

$$A = \frac{d^2\epsilon}{dv^2}, \qquad B = \frac{d^2\epsilon}{dvd\eta}, \qquad C = \frac{d^2\epsilon}{d\eta^2},$$

and then

$$\left(\frac{dp}{dt}\right)_v = -\frac{B}{C}, \qquad \left(\frac{dp}{dt}\right)_\eta = -\frac{A}{B}.$$

These two quantities are in general different but at the limit of stability they are equal and in particular at the critical point. Both these quantities are easy to measure. If we have coexistent phases the tangent plane is rolling on the surface with contact at two points and the successive positions intersect in the line giving the two points of contact and representing the different states in which the two phases can exist in different proportions at the same pressure and temperature. At the critical point according to van der Waals' equation.

$$\left(\frac{dp}{dt}\right)_v = \frac{R}{v-b} = \frac{R}{2b} \quad \text{and} \quad \frac{t_c}{p_c} = \frac{8b}{R}.$$

Hence

$$\left(\frac{dp}{dt}\right)_v \frac{t}{p} = \frac{d\log p}{d\log t} = 4. \tag{20}$$

Now we may experimentally determine the values of p and t for states of coexisting phases and make a graph in which we plot $\log p$ against $\log t$. If then van der Waals' equation were satisfied we should find that as we approached the critical point the slope of the curve approached 4. This value does not, as a matter of fact agree with that found by experiment, which points rather to 5 or 6 or 7. Various modifications of the equation have been proposed by Clausius and others. We could treat any of these proposals by similar methods. No entirely satisfactory equation of state has been proposed. The usefulness of the various forms depends on the particular inquiry to which they are applied.

Lecture XXVIII. Returning to van der Waals' law,

$$\left(\frac{dp}{dt}\right)_v = \frac{R}{v - b}.$$

This is not quite true, of course, but it is surprisingly correct in many cases over a very wide range. For very great densities it cannot be expected to hold, and we have to exclude dissociation at very high temperatures, and those states in which the substance is congealed. Now in the pt plane a line of constant volume becomes straight. It is easy to determine corresponding values of p and t under conditions of constant volume and observe how straight the curves in p against t are. At the limit of stability we had $(dp/dv)_t = 0$, i.e., maxima or minima of the isothermals in the pv plane. Keeping t constant in the pt-diagram corresponds to a vertical displacement. If $(dp/dv)_t > 0$ it is seen that the lines of increasing volume on the pt-diagram lie one above the other in the direction of increasing pressure; in the limit when $(dp/dv)_t = 0$ the successive lines of constant volume intersect. These lines will therefore envelop a locus which consists of points pv for which $(dp/dv)_t = 0$, i.e., for states at the limit of stability. This locus has a cusp which is the critical point. In the region within the cusp and near to it there are three tangent lines of the envelope through each point, i.e., for a given pair of values p, t there are three lines of constant volume along which one may proceed. Taking van der Waals' equation in the form (19), the equations

$$P = -\frac{3}{V^2} + \frac{\frac{8}{3}T}{V - 1/3}, \qquad \left(\frac{dP}{dV}\right)_T = \frac{6}{V^3} - \frac{\frac{8}{3}T}{(V - 1/3)^2} = 0$$

will give the cuspidal locus on elimination of V from

$$T = \frac{9(V - 1/3)^2}{4\,V^3}, \qquad P = -\frac{3}{V^2} + 6\,\frac{V - 1/3}{V^3} = \frac{3}{V^2} - \frac{2}{V^3}.$$

The plot of P against T is more readily made from this parametric form than from the equation obtained by eliminating V.

The point $P = 1$, $T = 1$ corresponding to $V = 1$ is the critical point. As

$$\left(\frac{dP}{dT}\right)_V = \frac{8/3}{V - 1/3}, \qquad \left(\frac{dP}{dT}\right)_{V=1} = 4.$$

The values of V, T, P and $(dP/dT)_V$ are entered in the table which clearly shows the cusp at (1, 1, 1) and from which the envelope may be plotted easily.

V	T	P	$(dP/dT)_V$
2/3	27/32 = .84	0	8
3/4	25/27 = .93	16/27 = .59	32/5
5/6	243/250 = .97	108/125 = .86	16/3
1	1	1	4
7/6	675/686 = .98	324/343 = .94	16/5
4/3	243/256 = .95	27/32 = .84	8/3
3/2	49/54 = .91	20/27 = .74	16/7
2	25/32 = .78	1/2 = .50	8/5
3	16/27 = .59	7/27 = .26	1
∞	0	0	0

Lecture XXIX. We return to the consideration of coexistent phases, basing the development upon the condition $\zeta_2 = \zeta_1$ or

$$\epsilon_2 - \epsilon_1 - t(\eta_2 - \eta_1) + p(v_2 - v_1) = 0.$$

For $\epsilon_2 - \epsilon_1$ we use (10); for $\eta_2 - \eta_1$ we use

$$\frac{dp}{dt} = \frac{\eta_2 - \eta_1}{v_2 - v_1} = \frac{Q}{t}\,\frac{1}{v_2 - v_1},$$

previously derived. Thus the condition may be given the form

$$\frac{\alpha}{pv_1v_2} - \frac{t}{p}\,\frac{dp}{dt} + 1 = 0.$$

But the three roots of van der Waals' equation for $p =$ const. satisfy

$$v^3 - \left(\frac{Rt}{p} + b\right)v^2 + \frac{\alpha}{p}v - \frac{\alpha\, b}{p} = 0,$$

and hence $v_1 v_2 v_3 = ab/p$ and

$$\frac{v_3}{b} = \frac{d \log p}{d \log t} - 1.$$

The value v_3 is that at which the rising (unstable) part of the isothermal cuts the horizontal line and is not attainable by experiment. But on substituting this in the equation we have

$$b^2 p + \frac{a}{\left(\frac{d \log p}{d \log t} - 1\right)^2} = \frac{b\,R\,t}{\frac{d \log p}{d \log t} - 2},$$

which is sometimes useful in working with coexistent phases when we are willing to put confidence in the equation of van der Waals.

The general equation of state

$$p = F'(v) + t f'(v),$$

of which van der Waals' is a special case, may be discussed. For this $(dp/dt)_v$ is again a function $f'(v)$ of v and at constant volume is constant, so that the isometric lines in the *pt*-diagram are straight. We have

$$\psi = -F(v) - t f(v) + \Phi(t),$$
$$\eta = f(v) - \Phi'(t),$$
$$\epsilon = -F(v) + \Phi(t) - t\,\Phi'(t).$$

If we use for $\Phi(t)$ the expression $ct - ct \log t$, then $\epsilon = -F(v) + ct$. At any rate both ϵ and η consist of a function of the volume plus a function of the temperature. It is to these equations that we naturally look for some improvement upon van der Waals'.

Lecture XXX. Let us make the hypothesis that there is an equation of state which is independent of the substance, provided only we measure p, v, t in the appropriate units. What results could be obtained? There is one state of the substance which is physically defined, namely, the critical state. It is therefore $P = p/p_c$, $V = v/v_c$, $T = t/t_c$ which are the variables which must be used and the equation must be between P, V, T. Such an expression as

$$\frac{\dfrac{pv}{t}}{\dfrac{p_c v_c}{t_c}} \text{ must be the same for all substances.}$$

If m denote the mass and M the molecular weight we have

$$\frac{p}{p_c},\ \frac{t}{t_c},\ \frac{v}{v_c},\ \frac{p_c v_c M}{t_c m},\ \frac{p\,v\,M}{tm}$$

equal for all substances. (The last two expressions must be measured in the same units for the different substances, but the first three may be measured in any units.) So, too,

$$\frac{t}{p}\left(\frac{dp}{dt}\right)_v = \frac{t}{p}\left(\frac{d\eta}{dv}\right)_t = \frac{1}{p}\left(\frac{dQ}{dv}\right)_t$$

would be alike. Also

$$\frac{t}{v}\left(\frac{dv}{dt}\right)_p = -\frac{t}{v}\left(\frac{d\eta}{dp}\right)_t = -\frac{1}{v}\left(\frac{dQ}{dp}\right)_t.$$

For coexistent phases there would be certain expressions invariant of the substance.

$$\frac{t}{p}\left(\frac{dp}{dt}\right)_v = \frac{1}{p}\left(\frac{dQ}{dv}\right)_t = \frac{t}{p}\,\frac{\eta_2 - \eta_1}{v_2 - v_1}.$$

As $\zeta_1 = \zeta_2$ we may state that the ratios

$$(\epsilon_2 - \epsilon_1) : t(\eta_2 - \eta_1) : p(v_2 - v_1)$$

are the same for all substances when 2 and 1 stand for the vapor and the liquid phase, each in the presence of an infinitesimal quantity of the other. By examining data for different substances one may see how far the departure from constancy is and thus gain some idea of in how far it might be hopeful to seek for equations of state which would satisfy the requirement that in proper units the equation should be the same for the different substances.

III. Further Notes on Gibbs' Lectures. Photographs of Models of the Thermodynamic Surface

These thirty lectures as given in the academic year 1899–1900 represent the development, discussion, and application of the matter in Papers I and II so far as Gibbs covered it. In the year 1901–1902 he covered the same ground in just fifteen lectures. He continued with a lecture on dynamical similarity and the theory of models which he applied to the consideration of intermolecular forces and the problem of corresponding states, and then launched into the topic of heterogeneous substances (Paper III). It will be seen that although he laid great stress on the physical and on the logical aspects of thermodynamics, and spent a good deal of time on van der Waals' equation as a type of equation of state, he did not indulge in many numerical applications, nor discuss practical engineering consequences of the theory. He used chiefly the pv-diagram, giving scant mention to the temperature entropy diagram.

An interesting and helpful episode in the course was the illustration of the discussion of the thermodynamic surface by a model of the surface for water, which had been sent him by Maxwell. Four photographs of this model taken from different points of view are reproduced here. The legends indicate the direction of the axes.

Maxwell's highly favorable comments on the work of Gibbs and the concrete evidence which he gave of his opinion through the construction of the model of the thermodynamic surface probably did more at the time to convince physicists of the importance of Gibbs's contributions than the reading of so long, so novel, so closely reasoned and withal so difficult a memoir as that on Heterogeneous Equilibrium. It is of interest in this connection to give the record of the award by the American Academy of Arts and Sciences of its Rumford Medal to Gibbs. At the meeting of May 25, 1880, Professor Lovering presented the following report from the Rumford Committee.*

"The mechanical theory of heat, which treats of heat as being, not a pecular kind of matter called caloric, but as being some form or forms of molecular motion, has made necessary and possible a new branch of mechanics, under the name of thermo-dynamics. This theory has not only introduced new ideas into science, but has demanded the application, if not the invention, of special mathematical equations. Clausius has devoted thirty years to the development of thermo-dynamics, and at the end of his ninth memoir he expresses, in two brief sentences, the

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* The Committee consisted of Wolcott Gibbs, E. C. Pickering, J. M. Ordway, John Trowbridge, J. P. Cooke, Joseph Lovering, G. B. Clark.

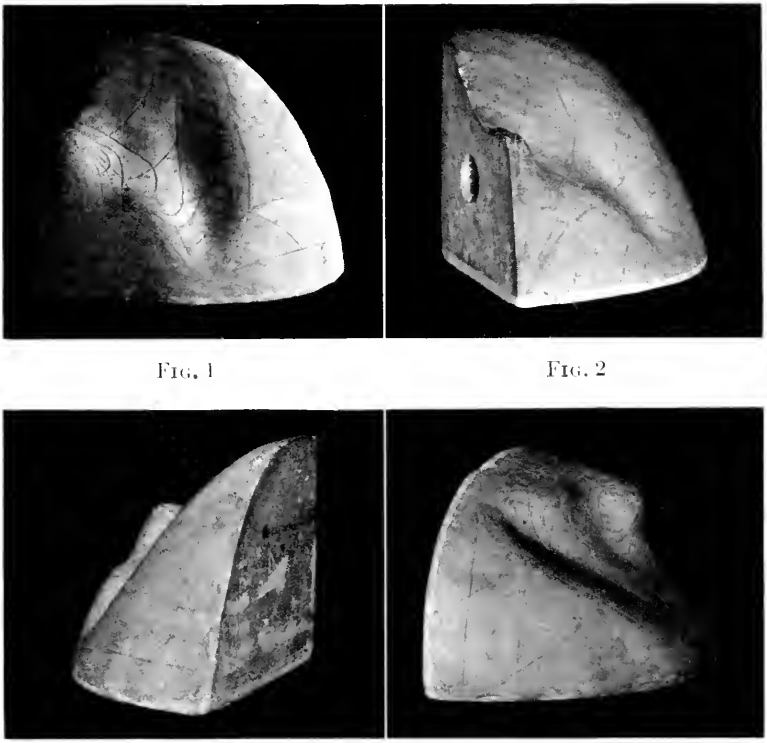

FIG. 1 FIG. 2

FIG. 3 FIG. 4

THE THERMODYNAMIC SURFACE (MAXWELL'S MODEL)

FIG. 1. Vertical axis; energy (ϵ). Axis of volume (v) toward the front and left. Axis of entropy (η) toward the right.

FIG. 2. Vertical axis; energy (ϵ). Axis of volume (v) toward the front and right. Axis of entropy (η) toward the right and back.

FIG. 3. Vertical axis; energy (ϵ). Axis of volume (v) toward rear and left. Axis of entropy (η) toward front and left.

FIG. 4. Vertical axis; volume (v). Axis of entropy (η) toward front and left. Axis of energy (ϵ) toward the right.

fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat: 1. The energy of the universe is constant; 2. The entropy of the universe tends towards a maximum.

"Professor J. Willard Gibbs, in his discussion of the 'Equilibrium of Heterogeneous Substances,' derives his criteria of equilibrium and stability from these two theorems of Clausius, and places the two generalizations of Clausius in regard to energy and entropy at the head of his first publication. Having derived from his criteria some leading equations, and having defined his sense of 'homogeneous' and its opposite, he applies these equations:—

"1. To the internal stability of homogeneous fluids.

"2. To heterogeneous masses, under the influence of gravity or otherwise; such as gas-mixtures, solids in contact with fluids, osmotic forces, capillarity, and liquid films.

"3. Finally, he considers the modifications introduced into the conditions of equilibrium by electromotive forces.

"His treatment of the subject is severely mathematical, and incapable of being translated into common language. The formulas, however, are not barren abstractions, but have a physical meaning.

"The laws of thermo-dynamics reach down to the heart of physics and extend their roots in all directions. It is now understood that the energy of a system of bodies depends on the temperature and physical state, as well as on the forms, motions, and relative positions of these bodies. The Rumford Committee congratulate the Academy on the opportunity they now enjoy of awarding the Rumford Premium for a contribution to physical science of far-reaching importance; not anticipating, but already realizing, the approval which this award must receive from all who are conversant with the subject.

"For the Committee,
"JOSEPH LOVERING, *Chairman.*"

The medal was awarded at the meeting of January 12, 1881, Professor Lovering having in the interim been elected president of the Academy. His address as Chairman of the Committee was in part* as follows.

"On the mechanical theory of heat, as a foundation, has been erected the grandest generalization of physical science, the Conservation of Energy. The results of observation and calculation agree, whenever a comparison is practicable, if the calculation is made upon the assumption that the totality of energy in a system, potential as well as dynamical, is as unchangeable as the totality of matter. This sweeping generalization includes and interprets Grove's experimental demonstration of the correlation and convertibility of the different forms of energy, known under the familiar names of gravity, elasticity, light, heat, electricity, magnetism, and chemical affinities. The conversion of heat (which is supplied to an indefinite amount by the consumption of the forests and the coal-beds) into ordinary mechanical energy or work, is of the highest significance to the advancing civilization of the race; but heat cannot be transformed into work without the transformation of a larger amount of heat of high temperature into heat of low temperature. This passage of heat from hot to cold bodies, without doing work, reinforced by the conduction and radiation of heat, creates the tendency to what is now called the dissipation of heat. This is what the writer in the *London Spectator* meant when he called heat the communist of the universe, the final consummation of this dissipation being a second chaos. Sir William Thomson has computed that the sun has lost through its radiations hundreds of times as much mechanical energy as is represented by the motions of all the planets. The energy thus dispensed to the solar system, and from it to remoter space, 'is dissipated, always more and more widely, through endless space, and never has been, and probably never can be, restored to the sun without acts as much beyond the scope of human intelligence as a creation or annihilation of energy, or of matter itself, would be.' Therefore, unless the sun has foreign supplies, in the fall of meteors or otherwise, where its drafts will be honored, its days are numbered.

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* The material here quoted is from *Proc. Amer. Acad. Arts Sci.*, **16,** pp. 407–408 and 417–421. The introductory portion which deals with the history of the award is omitted.

"What I have attempted to state in language as little technical as possible is tersely expressed by Clausius in two short sentences: 'The energy of the world is constant.' 'The entropy of the world (that is the energy not available for work) tends constantly towards a maximum.'

"Professor J. Willard Gibbs takes his departure from these two propositions when he enters upon his investigation on the 'Equilibrium of Heterogeneous Substances.' Any adequate theoretical treatment of this complex subject must be, necessarily, highly mathematical, and intelligible only to those familiar with the analytical theory of heat. To assist the imagination, Professor Gibbs has devised various geometrical constructions; especially one, of a curved surface, in which each point represents, through its three rectangular coördinates, the volume, energy, and entropy of a body in one of its momentary conditions.

The late Professor J. C. Maxwell (whose early death is ever a fresh grief to science) devoted thirteen pages of the fourth edition of his 'Treatise on Heat' to the elucidation and application of these constructions; and it is understood that he embodied in a visible model the equations in which Professor Gibbs expressed his strange surface. In a lecture delivered before the Chemical Society of London, Professor Maxwell gave publicly the endorsement of his great name to the merits of these researches which we are now met to honor. He says: 'I must not, however, omit to mention a most important American contribution to this part of thermo-dynamics by Professor Willard Gibbs, of Yale College, U. S., who has given us a remarkably simple and thoroughly satisfactory method of representing the relations of the different states of matter, by means of a model. By means of this model, problems which had long resisted the efforts of myself and others may be solved at once.'

"It is now my pleasant duty to present, in the name of the Academy and with their approving voice, the gold and silver medals to the Recording Secretary, Professor Trowbridge, who has been commissioned by Professor Gibbs to represent him on this occasion. I cannot but think that if Count Rumford were living, he would regard with peculiar pleasure this award. For the researches of Professor Gibbs are the consummate flower and fruit of seeds planted by Rumford himself, though in an unpromising soil, almost a century ago. In transmitting these medals to Professor Gibbs, by which the Academy desires to honor and to crown his profound scientific work, be pleased to assure him of my warm congratulations and the felicitations of all the Fellows of the Academy, here assembled to administer Count Rumford's Trust."

In reply to the President's address, the Recording Secretary then read the following letter from Professor Gibbs:—

"To THE AMERICAN ACADEMY OF ARTS AND SCIENCES:—

"*Gentlemen,*—Regretting that I am unable to be present at the meeting to which I have been invited by your President, I desire to express my appreciation of the very distinguished honor which you have thought fit to confer upon me. This mark of approbation of my treatment of questions in thermo-dynamics is the more gratifying, as the value of theoretical investigation is more difficult to estimate than the results obtained in other fields of labor. One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity. The success of the investigations in this respect is a matter on which he who makes them may be least able to form a correct judgment. It is, therefore, an especial satisfaction to find one's methods approved by competent judges.

"The leading idea which I followed in my paper on the Equilibrium of Heterogeneous Substances was to develop the *rôles* of energy and entropy in the theory of thermo-dynamic equilibrium. By means of these quantities the general condition of equilibrium is easily expressed, and by applying this to various cases we are led at once to the special conditions which characterize them. We thus obtain the consequences resulting from the fundamental principles of thermo-dynamics (which are implied in the definitions of energy and entropy) by a process which seems more simple, and which lends itself more readily to the solution of problems, than the usual method, in which the several parts of a cyclic operation are explicitly and separately considered. Although my results were in a large measure such as had previously been demonstrated by other methods, yet, as I readily obtained those which were to me before unknown, or but vaguely known, I was confirmed in my belief in the suitableness of the method adopted.

"A distinguished German physicist has said,—if my memory serves me aright,—that it is the office of theoretical investigation to give the form in which the results of experiment may be expressed. In the present case we are led to certain functions which play the principal part in determining the behavior of matter in respect to chemical equilibrium. The forms of these functions, however, remain to be determined by experiment, and here we meet the greatest difficulties, and find an inexhaustible field of labor. In most cases, probably, we must content ourselves at first with finding out what we can about these functions without expecting to arrive immediately at complete expressions of them. Only in the simplest case, that of gases, have I been able to write the equation expressing such a function for a body of variable composition, and here the equation only holds with a degree of approximation corresponding to the approach of the gas to the state which we call perfect.

"Gratefully acknowledging the very favorable view which you have taken of my efforts, I remain, gentlemen, very truly yours,

"J. WILLARD GIBBS.

"NEW HAVEN, Jan. 10, 1881."

It is noticeable that with the exception of mere mention of the chief divisions of the great memoir in the report recommending the award there is neither in the report nor in the address of the chairman any reference to the content of that memoir, let alone any critique of its importance to science; the references are to the previous state of thermodynamics and to the thermodynamic surface and Maxwell's model of it, i.e., to material by Gibbs contained in his Paper II, which we have been discussing. It may be recalled that in December 1878, more than two years prior to President Lovering's address, Gibbs had published in the *American Journal of Science* an Abstract of his memoir (Gibbs, I, Paper IV) from which certain important descriptive material might have been culled more readily than from the original. That the Rumford Committee realized that a great contribution had been made by Gibbs and that they promptly recognized it by their recommendation of the award of the medal is clear, but in how far they appreciated the nature and significance of the contribution is not indicated.*

Particularly interesting in the reply by Gibbs is his reference to the fact that it is only for gases that he has been able to write the equation expressing the thermodynamic functions for a body of variable composition. Perhaps his great attention in his course to van der Waals' equation was because, although its accuracy for liquid and vapor phases is not so great as that of the gas equation for gases, it offered some fair approximation to the representation of a decidedly less restricted state of matter and led to equations expressing the thermodynamic functions for more general bodies of variable composition. It is customary for the recipient of the medal to make a considerable address expounding as well as he can to a general academic audience the significance of some of his contributions. What would Gibbs have said about the memoir on Heterogeneous Equilibrium had he been able to be present? Would he have alluded to some of the important possible applications of his work on osmotic equilibrium or to the significance of his phase rule (obviously a matter easy to make graphic to the kind of audience he would have had) or would he have gone into the matter of the electrolytic cell, or the theory of dilute solutions, or the mass law? Perhaps he would have followed the lead of the address of the Chairman and confined himself chiefly to contributions of others.

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* In the first footnote of the Abstract (Gibbs, I, p. 358) Gibbs points out that Massieu "appears to have been the first to solve the problem of representing all properties of a body of invariable composition which are concerned in reversible processes by means of a single function"—a fact that was probably unknown to him at the time of printing Paper II.

It is not without interest that in the period from 1872 to 1891 he is not recorded as offering any course on thermodynamics which could be presumed to include any of the matters in his thermodynamic papers, although from 1886 on he announced a course on the *a priori* deduction of thermodynamic principles from the theory of probabilities, which in view of his paper of 1884 (Gibbs, II, Pt. II, p. 16) may safely be assumed to have dealt with statistical mechanics. Was he concentrating his attention, as Clausius and Maxwell had done and as Boltzmann and Kelvin were doing, on the attempt to deduce thermodynamic behavior from dynamical properties of matter and possibly to find some equation expressing the thermodynamic functions of a body of variable composition other than perfect gases? It is not often that we find a great scientist neglecting in his lectures his own most important contributions at a time when they are of as great interest to others as Gibbs' contributions were to the rising physical chemists of the decade from the early eighties to the early nineties of the past century. Certainly the subject matter of his Papers I and II to which he gave half his time during the year 1899–1900 in the course above summarized was no more difficult, no less suitable for instruction than the courses he did offer on mathematical physics to students who could not have been expected to have much if any physics beyond the first general course, or much if any mathematics beyond the differential and integral calculus.*

It has been seen that Gibbs, as he taught thermodynamics, late in his life, made much use of the pressure-volume diagram, discussed briefly the entropy-temperature and pressure-temperature diagrams, but ignored the volume-entropy diagram (except as its properties may be considered to be implied in those of the thermodynamic surface). He made no use of the concept of efficiency, so dear to the engineer, nor of that of availability of energy, upon which some authors base their discussion of entropy; as the equivalents of these ideas must be implied in any development of the subject, it is only the terminology and viewpoint, not the essentials, which were omitted. He dealt at length with the properties of the thermodynamic surface, but did not cover all the detail which was included in his second paper; there was no particular reason why all of it should be covered.

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* The list of courses offered by Gibbs from 1872 to the time of his death is given in my "Reminiscences of Gibbs by a Student and Colleague" in the *Scientific Monthly*, **32**, 210–227, (1931).

As for what we find in the current literature with respect to the subject matter of these two initial papers one may state that the temperature-entropy diagram is now treated at length in engineering treatises on the steam engine* in which many detailed illustrations, both graphical and numerical, may be found. Physicists and chemists do not seem to use the temperature-entropy diagram to any great extent. The thermodynamic surface was perhaps given more attention by Maxwell in his little book on *Heat* (4th edition) to which reference has been made than is now customary with writers of texts on the physics or chemistry of heat.† This neglect is certainly not due to any failure to appreciate the contributions of Gibbs any more than the failure to include in some modern treatise on mechanics many of the geometrical proofs of the *Principia* is an indication of the author's lack of appreciation of Newton. Science goes on its way, picking and choosing and modifying. The trend of the last fifty years is not toward Papers I and II. Interesting as they are historically, and important because of the preparation they afforded Willard Gibbs for writing his great memoir III, there is no present indication that they are in themselves significant for present or future science; for better or for worse we have adopted other ways of preparing for the exposition of the theory and for the use of the results of that memoir which in so many of its parts is indispensable today and in still others as yet inadequately explored may become indispensable in the future.

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* See for example the article on the Steam Engine in the *Encyclopedia Britannica* or the treatise *An Introduction to Thermodynamics for Engineering Students* by John Mills (Ginn and Co.) or *Thermodynamics of the Steam Engine and Other Heat Engines* by C. H. Peabody (John Wiley and Sons). It is far from clear that the use of the temperature-entropy diagram in such works derives directly from the presentation in Gibbs' Paper II.

† For example, in the excellent *Einführung in die theoretische Physik*, Berlin, 1921, Bd. II, Th. 1, by C. Schaefer, the theory of heat is presented in 562 pages. Yet the temperature-entropy diagram seems not to appear, nor the thermodynamic surface to be mentioned. There are fourteen references to Gibbs in the index, mentioning the following topics: The Gibbs paradox of increase of entropy on mixing gases, the total energy ϵ, the phase rule, definition of components, the electromotive force of a cell, and statistical mechanics. None of these references is to Paper I or II. In the *Thermodynamics* of G. N. Lewis and M. Randall, McGraw-Hill, 1923, there is equal citation of Gibbs for much the same topics but again no mention of the $t\eta$-diagram or thermodynamic surface.

D

THE GENERAL THERMODYNAMICAL SYSTEM OF GIBBS

[Gibbs, I, pp. 55–144; 419–424]

J. A. V. BUTLER

I. Introduction

1. General Thermodynamic Considerations. At the head of his memoir, "On the Equilibrium of Heterogeneous Substances," Gibbs quotes the first and second laws of thermodynamics, as stated by Clausius:

> "Die Energie der Welt ist constant.
> Die Entropie der Welt strebt einem Maximum zu."

From these two principles he proceeds to deduce, with rigor and in great detail, the conditions of equilibrium in heterogeneous systems containing any number of substances. As an introduction to his method, we shall first outline the earlier development of the laws of thermodynamics and discuss their bearing on the question of equilibrium in material systems.

The first law of thermodynamics, or the Principle of the Conservation of Energy, was first stated in a general form by Helmholtz in his memoir "On the Conservation of Force" (1847). Starting with a denial of the possibility of perpetual motion, and making use of the experimental results of Davy, Joule and Mayer on the production of heat by the expenditure of mechanical work and in the passage of electric currents through conductors, Helmholtz arrived at the generalisation that the sum of the energies of the universe is constant and when energy of one kind disappears, an equivalent amount of other kinds of energy takes its place.

Lord Kelvin, in 1851, introduced the concept of the intrinsic energy of a body as the sum of the total quantities of heat and work which can be obtained from it. Since it is not possible to remove the whole of the heat from a body, or to change it into a state in which we may be sure that no further work may be obtained from it, for practical purposes we may define a standard state in which the energy is taken as zero. Then the energy of a body in any given state is taken as the sum of the quantities of heat and work which must be supplied to bring the body from the standard state into the given state. The energy of a body or system of bodies in a given state is a definite quantity and is independent of the way in which it is brought into that state. For if it were possible for a system of bodies to have different amounts of energy in the same state, it would be possible to obtain energy without the system or any other bodies undergoing change, which is contrary to the Principle of Conservation of Energy.

Consider two states of a system in which its energy is ϵ' and ϵ''. The change of the energy of the system, i.e., the energy which must be supplied from outside, when it passes from the first to the second state, is $\Delta\epsilon = \epsilon'' - \epsilon'$. Since ϵ'' and ϵ' depend only on the initial and final states of the system, $\Delta\epsilon$ is independent of the way in which the change of state occurs. In general, the energy of a system may change (1) by receiving or giving heat to other bodies, and (2) by performing work against external forces. If, in a change of state, the system absorbs a quantity of heat Q from outside bodies and performs work W against external forces,* its energy change is

$$\Delta\epsilon = Q - W. \tag{1}$$

Now, although the energy change of a system in passing from a given initial state to a given final state is constant and independent of the way in which the change occurs, the same is not true of Q or W. But of the possible ways of conducting the change, there will usually be one for which W is a maximum and, therefore, Q also a maximum.

As a simple illustration, consider the fall of a body to the earth under the influence of gravity. When the body falls unimpeded no work is obtained and the whole of its energy is converted into heat when it collides with the earth. If we arrange a pulley so that, in its descent, the falling body raises another mass we shall obtain work corresponding to the weight of the mass raised. There is a limit to the amount of work which can be obtained in this way, for the first body will only continue to fall as long as its weight is greater than that of the body which is raised. The *maximum work* is obtained when the weight raised is only infinitesimally less than that of the falling body. In other words, we obtain the maximum work when the force tending to cause the change (in this case, the gravitational force on the falling body) is opposed by a force which is only smaller by an infinitesimal amount.

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* Heat evolved by the system and work done on the system by external forces are counted as negative.

Similar considerations apply to changes of other kinds. For example, in the expansion of a gas into an evacuated space, there is no opposing force and no work is obtained; but if the expansion of the gas is opposed by a mechanical force acting on a piston, work is obtained which has a maximum value when the force on the piston is only infinitesimally less than that required to balance the pressure of the gas. When the force on the piston exactly balances the gas pressure, no change occurs; but when the former is reduced by an infinitesimal amount the gas will expand and will continue to do so as long as the applied force is slightly less than that required to balance the gas pressure. Under these conditions we obtain the maximum work from the gas expansion. A change carried out in such a way is called a reversible change, since an infinitesimal increase in the forces opposing the change will be sufficient to make them greater than the forces of the system and will cause the change to proceed in the reverse direction.

If we take the system of bodies through a complete cycle of operations, so that its final state is identical with its original state, the total energy change is zero, so that by (1),

$$\Sigma Q - \Sigma W = 0 ;$$

i.e., the algebraic sum of all the quantities of heat absorbed by the system is equal to the algebraic sum of the amounts of work done against external forces.

In 1824 S.Carnot made use of such a process to determine the amount of work obtainable by an ideal heat engine, drawing heat from a heat reservoir at a temperature t' and giving it out at a lower temperature t''. In this process, the body or "working substance" is put through a cyclic series of operations, consisting of two isothermal and two adiabatic stages:

(1) The working substance is put in contact with the heat reservoir at the temperature t' and is allowed to expand, thereby performing work against the opposing forces and, since its temperature remains constant, absorbing a quantity of heat Q' from the heat reservoir.

(2) The working substance is thermally insulated so that it cannot receive or give up heat to its surroundings, and allowed to expand further, whereby work is obtained and the temperature falls to t''.

(3) The working substance is put in contact with a heat reservoir at t'', and is compressed until it reaches a state from which it can be brought into its original state without communication of heat. In this stage work is expended on the substance and a quantity of heat $-Q''$ passes from it to the heat reservoir.

(4) The working substance is thermally insulated, and brought into its original state by the expenditure of work.

In this process a quantity of heat Q' has been taken from the heat reservoir at t' and a quantity of heat $-Q''$ given to the heat reservoir at t''. Since the working substance has been returned into its original state the total work obtained is equal to the sum of the quantities of heat absorbed, i.e.

$$W = Q' + Q''.$$

The ratio of the work obtained to the heat absorbed at the higher temperature, i.e. $\dfrac{Q' + Q''}{Q'}$ is termed the *efficiency* of the process.

Carnot postulated, (1) that a cyclic process, in which every stage is carried out reversibly, must be more efficient than any irreversible cycle working between the same temperature limits can be, and (2) that all reversible cycles working between the same temperature limits must be equally efficient, whatever may be the nature of the working substance or of the change it undergoes. The proof of these propositions given by Carnot was unsatisfactory, for he adhered to the caloric theory of heat and did not admit that, when work is obtained, an equivalent amount of heat must disappear. Clausius, in 1850, showed that their proof, in fact, involves another principle which he stated as follows: "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature." Suppose that it were possible to have two such reversible cyclic processes, working between the same temperature limits, one of which was more efficient than the other. Then in the operation of the first process a quantity of heat Q_1 may be absorbed at the higher temperature and a quantity of work W obtained. This work may be used to operate the second process in the reverse direction so that it absorbs heat at the lower temperature and gives it out at the higher temperature. Let the amount of heat given out at the higher temperature for the expenditure of work W, in this cycle be Q_2. Then by hypothesis,

$$W/Q_1 > W/Q_2,$$

or,

$$Q_2 > Q_1.$$

Therefore the second cycle returns more heat to the heat reservoir at the higher temperature than is absorbed in the first cycle, and it would be possible by the use of the two cyclic processes, without the action of any outside agency, to cause heat to pass from the lower to the higher temperature, which is contrary to the principle stated above.

This principle is one of several alternative ways of stating the second law of thermodynamics. We may observe that the passage of heat from a hotter to a colder body is a spontaneous process by which a system, which is not in a state of equilibrium, proceeds towards equilibrium. Applied generally to all kinds of changes, the principle may be stated in the following way: Mechanical work can always be obtained when a system changes from a state, which is not a state of equilibrium, into a state of equilibrium. Conversely, it is impossible to obtain mechanical work, over and above the work expended from other sources, by the change of a system, which is in equilibrium, into another state.

We have seen that the maximum work is obtained from a spontaneous change when it is carried out by a reversible process. But a reversible process proceeds infinitely slowly, since at every stage the forces of the system are nearly balanced by opposing forces. When changes occur in Nature at a finite rate, the forces of the system must be appreciably greater than the opposing forces. Such changes are essentially irreversible and the maximum work of which they are capable, which Kelvin called the available energy, is not obtained. In an irreversible process only part of the available energy is obtained as work, the remainder is dissipated. Kelvin (1852) therefore stated the second law of thermodynamics as the Principle of the Dissipation of Energy:

"1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.

"2. Any *restoration* of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organised matter, either endowed with vegetable life or subjected to the will of an animated creature."

To return to Carnot's cycle, Kelvin had pointed out in 1848 that Carnot's theorem may be employed to define an absolute scale of temperature. Since the ratio of the work obtained in a reversible Carnot cycle to the heat absorbed at the higher temperature depends solely on the temperatures of the two bodies between which the transfer of heat is effected, we may write

$$\frac{W}{Q'} = \phi(t', t''),$$

where $\phi(t', t'')$ is a function of t' and t'' alone. Kelvin defined absolute temperature so that

$$\phi(t', t'') = \frac{t' - t''}{t'}.$$

Then,

$$W/Q' = \frac{Q' + Q''}{Q'} = \frac{t' - t''}{t'};$$

so that,

$$\frac{Q''}{Q'} = -\frac{t''}{t'},$$

and therefore,

$$\frac{Q'}{t'} + \frac{Q''}{t''} = 0;$$

i.e. the sum of the quantities of heat absorbed by the working substance in a reversible Carnot cycle, each divided by the absolute temperature at which it takes place, is zero. In 1854, Kelvin and Clausius independently showed that this result may be extended to any reversible cyclic process whatever, since any reversible cyclic process whatever may be resolved into a number of simple Carnot cycles. Thus, we may write:

$$\oint \frac{dQ}{t} = 0,$$

where dQ is the element of heat absorbed at the temperature t in any reversible cycle, and the integration is extended round the cycle.

Let us now designate by A and B two reversible paths by which a body or system of bodies may be brought from a state (I) to a state (II). We may take the system through a reversible cycle by changing it from state (I) to state (II) by path A and returning it to its original state (I) by path B. Therefore,

$$\left.\int_{(I)}^{(II)} \frac{dQ}{t}\right]_A + \left.\int_{(II)}^{(I)} \frac{dQ}{t}\right]_B = 0$$

or, by changing the direction of the second term,

$$\left.\int_{(I)}^{(II)} \frac{dQ}{t}\right]_A = \left.\int_{(I)}^{(II)} \frac{dQ}{t}\right]_B.$$

The integral, $\int_{(I)}^{(II)} dQ/t$ has therefore the same value for all reversible paths by which the system may be changed from state (I) to state (II). Its value for a reversible path is thus a definite quantity, depending only on the initial and final states of the system, and it may be regarded as the difference between the values of a function of the state of the system in the two states considered. This function was termed the *entropy* of the system by Clausius in 1855. We may therefore write:

$$\int_{(I)}^{(II)} \frac{dQ}{t} = \eta^{II} - \eta^{I}, \tag{2}$$

where η^I and η^{II} are the values of the entropy in states (I) and (II).

For an infinitesimal change of state, (1) may be written in the form:

$$d\epsilon = dQ - dW.$$

Now if the change of state is reversible, according to (2), $dQ = td\eta$; also if the work is done by an increase of volume dv against a pressure p, $dW = pdv$, so that

$$d\epsilon = td\eta - pdv. \tag{3}$$

We may observe that all infinitesimal changes of state of a system, which is in equilibrium, fulfil the condition of reversibility, for equilibrium is a state in which the forces of the system are balanced by the opposing forces, and in an infinitesimal change the system can only be removed to an infinitesimal extent from a state of equilibrium. Equation (3) therefore applies generally to infinitesimal changes of a system which is in a state of equilibrium.

We will now consider the changes of a system of bodies in relation to the changes which necessarily occur in surrounding bodies. When the sytem undergoes a reversible change from a state (I) to a state (II), the entropy change, as we have seen, is:

$$\eta^{II} - \eta^{I} = \int_{(I)}^{(II)} dQ/t,$$

where dQ is the element of heat absorbed at temperature t. This heat must come from surrounding bodies, and the process can only be perfectly reversible when each element of heat is absorbed from a body which has the same temperature as the system itself. Therefore $-\int_{(I)}^{(II)} dQ/t$ represents the entropy change of the surrounding bodies, so that when a reversible change takes place the sum of the changes of entropy of the system and its surroundings is zero.

On the other hand, if the change of the system is irreversible, its entropy change is still $\eta^{II} - \eta^{I}$, since this quantity depends solely on the initial and final states and not on the way in which the change occurs, but it is no longer equal to $\int_{(I)}^{(II)} dQ/t$. Since less work is obtained from the system in an irreversible change than in a reversible change, the heat absorbed is also less, and therefore:

$$\int_{(I)}^{(II)} dQ/t_{\ (system)} < \eta^{II} - \eta^{I}$$

or

$$\eta^{II} - \eta^{I} - \int_{(I)}^{(II)} dQ/t_{\ (system)} > 0.$$

The decrease in entropy of the surroundings cannot be greater than $\int_{(I)}^{(II)} dQ/t_{\ (system)}$, since an element of heat dQ can only be absorbed from a body having a temperature equal to or greater than the momentary temperature t of the system. The total entropy change of the system and its surroundings is therefore positive, i.e. when an irreversible change takes place, the entropy of the universe is increased. We have seen that irreversible changes may take place spontaneously in the universe or in any isolated system which is not in a state of equilibrium, so that we arrive at Clausius' statement of the second law of thermodynamics; "The entropy of the universe tends to a maximum."

It is evident that the second law of thermodynamics affords a criterion of equilibrium, which may be stated in several different ways. The statement of Clausius, that the entropy of an isolated system tends to a maximum, implies that equilibrium is reached when the entropy has the maximum value which is consistent with its energy, and when there is no possible change, the energy remaining constant, which can cause a further increase of entropy.

Also, the entropy of a system remains constant if the latter does not undergo any irreversible changes and if it does not receive any heat from its surroundings. Any change of its energy under these conditions must be the result of work done on or by the system against external forces. We have seen that if a system is not in equilibrium, it may undergo changes from which work can be obtained and which therefore result in a decrease of energy. A system is therefore in equilibrium, if there is no possible change, which does not involve a change of entropy, whereby its energy can be decreased.

In making use of these criteria of equilibrium we need only consider infinitesimal changes, for every finite change must begin by being an infinitesimal one and if no infinitesimal change is possible it is evident that no finite change can occur. If $(\delta\eta)_\epsilon$, $(\delta\epsilon)_\eta$ represent the change of entropy and energy in any infinitesimal change of the system in which the energy and entropy respectively remain constant, the two criteria of equilibrium stated above may be expressed by the statement that

$$(\delta\eta)_\epsilon \leqq 0 \text{ and } (\delta\epsilon)_\eta \geqq 0,$$

for all possible changes.

Gibbs first discusses in detail the equivalence and validity of these criteria, and the conditions to be observed in using them. An analysis of his discussion is given in the following chapter, but the reader who does not wish, at this stage, to consider these elaborate arguments need only read Section 4 on the Interpretation of the Conditions and may then proceed to the discussion of their application which begins with Chapter III.

II. The Criteria of Equilibrium and Stability

2. The Criteria. Gibbs begins his discussion of the equilibrium of heterogeneous substances by stating in the following propositions the criterion of equilibrium for a material system which is isolated from all external influences:

I. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.*

This condition of equilibrium may be written

$$(\delta\eta)_\epsilon \leqq 0, \qquad (4)\ [1]$$

where $(\delta\eta)_\epsilon$ denotes a variation of entropy, the energy remaining constant.

II. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.*

This condition may be written

$$(\delta\epsilon)_\eta \geqq 0, \qquad (5)\ [2]$$

where $(\delta\epsilon)_\eta$ denotes a variation of energy, the entropy remaining constant.

He proceeds to prove, that these two propositions are equivalent to each other, that they are sufficient for equilibrium, and that they are necessary for equilibrium. We shall quote largely from Gibbs' own exposition, interpolating explanatory remarks where they seem to be helpful.

*3. Equivalence of the Two Criteria.** "It is always possible to increase both the energy and the entropy of the system, or to decrease both together, viz., by imparting heat to any part of the system or by taking it away. For, if condition I is not satisfied, there must be some variation in the state of the system for which

$$\delta\eta > 0 \text{ and } \delta\epsilon = 0.\text{''}$$

Therefore, by taking heat from the system in its varied state we may decrease the entropy to its original value and at the same time diminish the energy, so that we reach a state for which

$$\delta\eta = 0 \text{ and } \delta\epsilon < 0.$$

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* Gibbs, I, p. 56, lines 20–37.

Thus, if there are possible variations which do not satisfy I, there must also be possible variations which do not satisfy II. Thus if condition I is not satisfied, condition II is not satisfied. Conversely, it is shown that if condition II is not satisfied, condition I is not satisfied, so that the two conditions are equivalent to each other.

*4. Interpretation of the Conditions.** Before proceeding to the proof of the sufficiency and necessity of the criteria of equilibrium, Gibbs discusses the interpretation of the terms in which the criteria are expressed.

In the first place, "equations which express the condition of equilibrium, as also its statement in words, are to be interpreted in accordance with the general usage in respect to differential equations, that is, infinitesimals of higher orders than the first relatively to those which express the amount of change of the system are to be neglected." That is, if $\delta\epsilon$ is change in the energy produced by a change δS in the state of the system, and if $d\epsilon/dS$ is the limiting value of $\delta\epsilon/\delta S$ when δS becomes infinitely small, the value of $\delta\epsilon$ is taken as $(d\epsilon/dS)\cdot\delta S$, infinitesimals of higher orders, such as $d^2\epsilon/dS^2$, being neglected. But different kinds of equilibrium may be distinguished by noting the actual values of the variations. The sign Δ is used to indicate the value of a variation, when infinitesimals of the higher orders are not neglected. Thus, $\Delta\epsilon$ is the actual energy change produced by a small, but finite variation in the state of the system. The conditions of the different kinds of equilibrium may then be expressed as follows; for stable equilibrium

$$(\Delta\eta)_\epsilon < 0, \qquad \text{i.e., } (\Delta\epsilon)_\eta > 0, \tag*{(6) [3]}$$

(i.e. the entropy is a maximum at constant energy and the energy a minimum at constant entropy for all possible variations); for neutral equilibrium there must be some variations in the state of the system for which

$$(\Delta\eta)_\epsilon = 0, \qquad \text{i.e., } (\Delta\epsilon)_\eta = 0; \tag*{(7) [4]}$$

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* Gibbs, I, p. 56, line 38; p. 58, line 40.

(i.e. which do not change the entropy at constant energy, or the energy at constant entropy), while in general

$$(\Delta\eta)_\epsilon \leqq 0, \qquad \text{i.e. } (\Delta\epsilon)_\eta \geqq 0; \tag*{(8) [5]}$$

and for unstable equilibrium there must be some variations for which

$$(\Delta\eta)_\epsilon > 0, \tag*{(9) [6]}$$

i.e. there must be some for which

$$(\Delta\epsilon)_\eta < 0,\text{''} \tag*{(10) [7]}$$

(i.e. in respect to some variations the entropy has the properties of a minimum, and the energy of a maximum), while the general criteria of equilibrium:

$$(\delta\eta)_\epsilon \leqq 0, \qquad \text{i.e. } (\delta\epsilon)_\eta \geqq 0; \tag*{(11) [8]}$$

are still satisfied.

Secondly, in these criteria of equilibrium only *possible* variations are taken into account. Changes of state involving the transport of matter through a finite distance are excluded from consideration, so that an increase in the quantity of matter in one body at the expense of that in another, is regarded as possible only when the two bodies are in contact. If the system consists of parts between which there is supposed to be no thermal communication, the entropy of each part is regarded as constant, since no diminution of entropy of any of these parts is possible without the passage of heat. In this case the condition of equilibrium becomes

$$(\delta\epsilon)_{\eta', \eta'', \text{ etc.}} \geqq 0, \tag*{(12) [9]}$$

where η', η'', etc. denote the entropies of the various parts between which there is no communication of heat.

Otherwise, "only those variations are to be rejected as impossible, which involve changes which are prevented by passive forces or analogous resistances to change." It is necessary to consider what is meant by this limitation.

Systems are frequently met with which are not in equilibrium, yet which appear to remain unchanged for an unlimited time. Thus, a mixture of hydrogen and oxygen appears to remain unchanged, although it is not in a true state of equilibrium, for a small cause such as an electric spark may cause a change out of all proportion to its magnitude. In such a case the change of the system into a state of equilibrium is supposed to be prevented by "passive forces or resistance to change," the nature of which is not well understood. It is evident that only those forces or resistances which are capable of *preventing* change need be considered. Those like viscosity, which only retard change, are not sufficient to make impossible a variation which they influence.

The existence of such passive resistances to change can easily be recognised. Thus, it is possible that a system composed of water, oxygen and hydrogen which is not in equilibrium with regard to changes involving the formation of water, will remain unchanged for an indefinite period. This equilibrium can be distinguished from that caused by "the balance of the active tendencies of the system," i.e., when the tendency of hydrogen and oxygen to combine is balanced by the tendency of water to dissociate, for whereas in the former case we may vary the quantities of any of the substances, or the temperature or pressure without producing any change in the quantity of water present in the system; in the latter case an infinitesimal change in the state of the system will produce a change in the amount combined.

Thus if we regard variations involving the combination of hydrogen and oxygen as prevented by the passive forces or resistances, and therefore impossible, we may still apply the conditions of equilibrium to discover the equilibrium state of a system containing given amounts of hydrogen, oxygen and water under these conditions.

5. Sufficiency of the Criteria of Equilibrium.[*] Three cases are considered, corresponding to the three kinds of equilibrium.

(a) "If the system is in a state in which its entropy is greater than in any other state of the same energy, it is evidently in equilibrium, as any change of state must involve either a decrease of entropy or an increase of energy, which are alike impossible for an isolated system. We may add that this is a case of *stable* equilibrium, as no infinitely small cause (whether relating to a variation of the initial state or to the action of external bodies) can produce a finite change of state, as this would involve a finite decrease of entropy or increase of energy."

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[*] Gibbs, I, p. 58, line 41–p. 61, line 11.

(b) "The system has the greatest entropy consistent with its energy, and therefore the least energy consistent with its entropy but there are other states of the same energy and entropy as its actual state."

Gibbs first shows by special arguments that in this case the criteria are sufficient for equilibrium in two respects. In the first place, "it is impossible that any motion of masses should take place; for if any of the energy of the system should come to consist of *vis viva* (of sensible motions), a state of the system identical in other respects but without the motion would have less energy and not less entropy, which would be contrary to the supposition." It is evident that if this last state is impossible, a similar state in which the parts of the system are in motion is equally impossible, since the motion of *appreciable* parts of the system does not change their nature.

Secondly, the passage of heat from one part of the system to another, either by conduction or radiation, cannot take place, as heat only passes from bodies of higher to those of lower temperature, and this involves an increase of entropy.

The criteria are therefore sufficient for equilibrium, so far as the motion of the masses and the transfer of heat are concerned. In order to justify the belief that the condition is sufficient for equilibrium in every respect, Gibbs makes use of the following considerations.

"Let us suppose, in order to test the tenability of such a hypothesis, that a system may have the greatest entropy consistent with its energy without being in equilibrium. In such a case, changes in the state of the system *must take place*, but these will necessarily be such that the energy and entropy remain unchanged and the system will continue to satisfy the same condition, as initially, of having the greatest entropy consistent with its energy." Now the change we suppose to take place cannot be infinitely slow, except at particular moments, so that we may choose a time at which it is proceeding at a finite rate. We will consider the change which occurs in a short interval of time after the chosen time. No change whatever in the state of the system, which does not alter the value of the energy, and which commences in the same state which the system has at the chosen time, will cause an increase of entropy. "Hence, it will generally be possible by some slight variation in the circumstances of the case" (e.g., by a slight change of pressure or temperature or of the quantities of the substances) "to make all changes in the state of the system like or nearly like that which is supposed actually to occur, and not involving a change of energy, to involve a necessary decrease of entropy, which would render any such change impossible." "If, then, there is any tendency toward change in the system as first supposed, it is a tendency which can be entirely checked by an infinitesimal variation in the circumstances of the case. As this supposition cannot be allowed, we must believe that a system is always in equilibrium when it has the greatest entropy consistent with its energy, or, in other words, when it has the least energy consistent with its entropy."

The essential steps of this argument may be recapitulated as follows. A system having the greatest entropy consistent with its energy must be in equilibrium, because

(α) if it were not in equilibrium a change must take place, and except at particular moments must take place at a finite rate;

(β), but it is shown that in such a case, the change can be entirely checked by an infinitely small modification of the circumstances of the case;

(γ), therefore, an infinitely small modification makes a finite difference in the rate of change, which cannot be allowed.

We may observe that the statement that the hypothetical change cannot be infinitely slow is an essential part of the argument. For, if the change which is supposed to occur were infinitely slow, there would be no reason to disallow it because it can be entirely checked by an infinitely small modification of the case. The argument depends finally on the consideration that an infinitely small modification of the circumstances cannot cause a finite change in the rate of change of the system, for as is explicitly stated in a succeeding paragraph, this is "contrary to that continuity we have reason to expect."

"The same considerations will evidently apply to any case in which a system is in such a state that $\Delta\eta \leqq 0$ for any *possible* infinitesimal variation of the state for which $\Delta\epsilon = 0$, even if the entropy is not the greatest of which the system is capable with the same energy." Thus a system of hydrogen, oxygen and water is in equilibrium when $(\Delta\eta)_\epsilon \leqq 0$, for all *possible* variations, even if the entropy is not the greatest for the same amount of energy. The conditions may be such that the combination of hydrogen and oxygen to water would cause an increase of entropy in the isolated system, but if this change is prevented by passive forces or resistances to change, variations involving it are not possible, and the system is in equilibrium if $(\Delta\eta)_\epsilon \leqq 0$, for all variations which do not involve such changes.

(c) When "$\delta\eta \leqq 0$ for all possible variations not affecting the energy, but for some of these variations $\Delta\eta > 0$, that is, when the entropy has in some respects the characteristic of a minimum."

"In this case the considerations adduced in the last paragraph will not apply without modification, as the change of state may be infinitely slow at first, and it is only in the initial state that $(\delta\eta)_\epsilon \leqq 0$ holds true." None of the differential coefficients of all orders of the quantities which determine the state of the system, taken with respect to the time, can have any value other than 0, for the state of the system for which $(\delta\eta)_\epsilon \leqq 0$. For if some of them had finite values, "as it would generally be possible, as before, by some infinitely small modification of the case, to render impossible any change like or nearly like that which might be supposed to occur, this infinitely small modification of the case would make a finite difference in the value of differential coefficients which had before the finite values, or in some of lower orders, which is contrary to that continuity which we have reason to expect. Such considerations seem to justify us in regarding such a state as we are discussing as one of theoretical equilibrium; although as the equilibrium is evidently unstable, it cannot be realized."

The argument of the last section is here applied to the higher differential coefficients of the quantities which represent the state of the system with respect to the time. Thus if S is one of the quantities representing the state of the system, it is shown that all such differential coefficients as

$$\frac{dS}{dt}, \qquad \frac{d^2S}{dt^2}, \qquad \frac{d^3S}{dt^3}, \qquad \text{etc.},$$

are zero in the state for which $(\delta\eta)_\epsilon \leqq 0$.

It is evident that the system cannot be in equilibrium unless all these quantities have the value 0, for if dS/dt is zero in the initial state and one of the higher coefficients has a finite value, dS/dt will have a finite value at a subsequent time. The proof that they are zero in the state for which $(\delta\eta)_\epsilon \leqq 0$ may be stated in greater detail as follows. If any of the differential coefficients have finite values, the system must undergo a change, which, however, may be infinitely slow so long as $(\delta\eta)_\epsilon \leqq 0$. But, by an infinitesimal modification in the circumstances, it will be possible to produce a state for which $(\delta\eta)_\epsilon < 0$. Such changes will then be impossible. That is, an infinitely small modification of the circumstances will cause a finite change in the values of those differential coefficients which previously had finite values. But this is regarded as impossible. The system can therefore continue unchanged in the state for which $(\delta\eta)_\epsilon \leqq 0$, which must be regarded as a state of equilibrium, but since there are changes for which $(\Delta\eta)_\epsilon > 0$, it is evidently a state of unstable equilibrium.

6. *Necessity of the Criteria of Equilibrium.*[*] When "the active tendencies of the system are so balanced that changes of every kind, except those excluded in the statement of the condition of equilibrium, can take place *reversibly* (i.e., both in the positive and the negative direction,) in states of the system differing

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[*] Gibbs, I, p. 61, line 11; p. 62, line 8.

infinitely little from the state in question", the criteria are evidently necessary for equilibrium. For if there is any possible change for which $(\delta\eta)_\epsilon \leqq 0$ does not hold, since no passive forces or resistances to change are operative, this change will take place. Also, in this case, the inequality in the equations cannot apply, since for every change of the system there is a similar one of opposite sign, so that if for a certain change of state $(\delta\eta)_\epsilon < 0$ we should have $(\delta\eta)_\epsilon > 0$ for a similar change of opposite sign. In this case, we may therefore omit the sign of inequality and write as the condition of equilibrium

$$(\delta\eta)_\epsilon = 0, \qquad \text{i.e. } (\delta\epsilon)_\eta = 0. \qquad (13)\ [10]$$

"But to prove that the condition previously enunciated is in every case necessary, it must be shown that whenever an isolated system remains without change, if there is any infinitesimal variation in its state, not involving a finite change of position of any (even an infinitesimal part) of its matter, which would diminish its energy . . . without altering its entropy, . . . this variation involves changes in the system which are prevented by its passive forces or analogous resistance to change. Now, as the described variation in the state of the system diminishes its energy without altering its entropy, it must be regarded as theoretically possible to produce that variation by some process, perhaps a very indirect one, so as to gain a certain amount of work (above all expended on the system)." We have seen that according to the second law of thermodynamics, a change which can be made to yield work may take place spontaneously, and will do so unless prevented by passive forces. "Hence we may conclude that the active forces or tendencies of the system favor the variation in question, and that equilibrium cannot subsist unless the variation is prevented by passive forces."

III. Definition and Properties of Fundamental Equations*

7. The Quantities ψ, ζ, χ. At this point, Gibbs proceeds to apply the criterion of equilibrium to deduce the laws which determine equilibrium in heterogeneous systems. For this purpose he uses the criterion in its second form, "both because it admits more readily the introduction of the condition that there shall be no thermal communication between the different parts of the system, and because it is more convenient, as respects the form of the general equations relating to equilibrium, to make the entropy one of the independent variables which determine the state of the system, than to make the energy one of these variables."* In order to apply the criterion it is necessary to specify completely the possible variations of which the energy of the system is capable, and for this purpose differential coefficients, representing the change of energy of homogeneous parts of the system with the quantities of their component substances, must be introduced. The complete significance of these quantities does not appear until a later stage. It is thought that the discussion of the conditions of equilibrium in heterogeneous systems will be more easily followed if we first define the auxiliary functions ψ, ζ and χ and derive the variations of the energy, and of these quantities, in homogeneous masses.

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* Gibbs, I, 85–92.

Let ϵ, η and v be the energy, entropy and volume respectively of a homogeneous body at a temperature t and pressure p. We have seen that in any given state the energy and entropy of a body are definite, but since it is only possible to measure *differences* of energy and entropy, "the values of these quantities are so far arbitrary, that we may choose independently for each simple substance, the state in which its energy and entropy are both zero. The values of the energy and entropy of any compound body in any particular state will then be fixed. Its energy will be the sum of the work and heat expended in bringing its components from the states in which their energies and their entropies are zero into combination and to the state in question; and its entropy is the value of the integral $\int \frac{dQ}{t}$ for any *reversible* process by which that change is effected."

The quantities ψ, ζ and χ, defined by the equations

$$\psi = \epsilon - t\eta, \qquad (14)\ [87]$$

$$\zeta = \epsilon - t\eta + pv, \qquad (15)\ [91]$$

$$\chi = \epsilon + pv; \qquad (16)\ [89]$$

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* Gibbs, I, 62.

have then definite numerical values in any state of the homogeneous body.

The definition

$$\psi = \epsilon - t\eta \qquad (17)\ [105]$$

may evidently be extended to any material system whatever which has a uniform temperature throughout. Consider two states of the system at the same temperature, in which ψ has the values ψ' and ψ''. The decrease in ψ in the change from the first to the second state is

$$\psi' - \psi'' = \epsilon' - \epsilon'' - t(\eta' - \eta''). \qquad (18)\ [106]$$

Now if the system is brought from the first to the second state by a reversible process in which a quantity of work W is done by the system and a quantity of heat Q absorbed, the decrease of energy is:

$$\epsilon' - \epsilon'' = W - Q, \qquad (19)\ [107]$$

and since the process is reversible;

$$Q = t(\eta'' - \eta'), \qquad (20)\ [108]$$

so that;

$$\psi' - \psi'' = W; \qquad (21)\ [109]$$

i.e. the decrease in ψ, in a change of state at constant temperature, is equal to the work done by the system when the change of state is carried out by a reversible process. Thus ψ can be regarded as the maximum work function of the system for changes at constant temperature. Equation (21) can be written as:

$$-(\Delta\psi)_t = W, \qquad (22)$$

so that, for an infinitesimal reversible change of state, we may write:

$$-(\delta\psi)_t = dW. \qquad (23)\ [110]$$

In mechanics the potential ϕ of a particle in a field of force is a quantity such that the work obtained in a small displacement of the particle is

$$dW = -d\phi.$$

If the forces acting on the particle in the directions of the x, y, and z axes are f_1, f_2, f_3 the work obtained in a small displacement is

$$dW = -d\phi = f_1 dx + f_2 dy + f_3 dz,$$

so that

$$f_1 = \frac{\partial(-\phi)}{\partial x}, \qquad f_2 = \frac{\partial(-\phi)}{\partial y}, \qquad \text{etc.}$$

The forces acting on the particle are thus differentials of $-\phi$, and $-\phi$ is the force function of the particle. The quantity ψ has analogous properties and, according to (23), $-\psi$ is the force function of the system for changes at constant temperature.

A system is in equilibrium at constant temperature if there is no possible change of state which could yield work, that is, for which dW is positive, and therefore $\delta\psi$ negative. Thus, we may write as the condition of equilibrium for a system which has a uniform temperature throughout:

$$(\delta\psi)_t \geqq 0; \qquad (24)\ [111]$$

that is, the variation of ψ for every possible change which does not affect the temperature is either positive or zero. Gibbs gives a direct proof that the condition of equilibrium (24) is equivalent to the condition (5) when applied to a system which has a uniform temperature throughout, for which the reader may be referred to the original memoir.* The definition

$$\zeta = \epsilon - t\eta + pv \qquad (25)\ [116]$$

may similarly be extended to any material system whatever which has a uniform temperature and pressure throughout. We will consider two states of the system, at the same temperature and pressure, in which ζ has the values ζ' and ζ''. The decrease in ζ in the change of the system from the first to the second state is,

$$\zeta' - \zeta'' = \epsilon' - \epsilon'' - t(\eta' - \eta'') + p(v' - v''). \qquad (26)$$

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* Gibbs, I, 90. See also this volume, page 214.

Now, if the system is brought from the first to the second state by a reversible process in which work W is done by the system and heat Q absorbed, we have as before

$$\epsilon' - \epsilon'' = W - Q,$$
$$Q = t(\eta'' - \eta'),$$

so that

$$\zeta' - \zeta'' = W + p(v' - v'') = W - p(v'' - v'). \tag{27}$$

Now $p(v'' - v')$ is the work done by the system in increasing its volume from v' to v'' at the constant pressure p, and the quantity

$$W - p(v'' - v') = W',$$

i.e., the maximum work of the change at constant temperature and pressure less the work done on account of the change of volume, is often known as the "net work" of the change. Just as the decrease in ψ in a change at constant temperature is equal to the maximum work obtainable, the decrease in ζ in a change at constant temperature and pressure is equal to the "net work" obtainable. Thus ζ is the "net work function" of the system. From considerations similar to those cited in discussing ψ, it can be seen that $-\zeta$ is the force function of the system for constant temperature and pressure.

Equation (27) may be written in the form

$$-\Delta\zeta = W', \tag{28}$$

so that, for an infinitesimal reversible change of state, we may write

$$-(\delta\zeta)_{t,p} = dW'. \tag{29}$$

Now, a system is in equilibrium at constant temperature and pressure if there is no possible change of state for which the net work is positive. We may therefore write as a criterion of equilibrium;

$$(\delta\zeta)_{t,p} \geqq 0, \qquad (30)\ [117]$$

that is, a system is in equilibrium when the variation of ζ for every possible change of state, which does not affect the temperature and pressure, is zero or positive. It follows that it is necessary for the equilibrium of two masses of the same composition, e.g., water and ice, which are in contact, that the values of ζ for equal quantities of the two masses must be equal. Thus, if the value of ζ for unit mass of ice were greater than the value of ζ for unit mass of water, at the temperature and pressure at which they are in equilibrium with one another, the value of ζ of the system could be decreased by the change, ice → water, at constant temperature and pressure. Since according to (30) this is impossible, the values of ζ for unit masses of ice and water in equilibrium with each other, must be equal. Similarly for the equilibrium of three masses, one of which can be formed out of the other two, it is necessary that the value of ζ for the first mass should be equal to the sum of the values of ζ for those quantities of the other masses, out of which the first mass can be formed. For example, 100 grams of calcium carbonate can be formed from 56 grams of lime and 44 grams of carbon dioxide. When the three substances are in equilibrium with each other, the value of ζ for 100 grams of calcium carbonate must be equal to the sum of the values of ζ for 56 grams of lime and 44 grams of carbon dioxide. Also if a solution composed of a parts of water and b parts of a salt is in equilibrium with crystals of the salt and with water vapor, the value of ζ for the quantity $a + b$ of the solution is equal to the sum of the values of ζ for the quantities a of water vapor and b of the salt.

The definition

$$\chi = \epsilon + pv \tag{31}$$

may likewise be extended to any material system for which the pressure is uniform throughout. If we consider two states of a system at the same pressure, in which χ has the values χ' and χ'', we see that

$$\chi'' - \chi' = \epsilon'' - \epsilon' + p(v'' - v'), \qquad (32)\ [119]$$

or

$$\Delta\chi = \Delta\epsilon + p\Delta v = Q_p, \tag{33}$$

i.e., the heat absorbed in a change which occurs at constant pressure, when the only work done is that due to increase in volume, is equal to the increase of χ.

Similarly, when a system undergoes a change at constant volume, $p\Delta v$ is zero and, if no work is done against external forces other than the pressure, the increase of energy is equal to the heat absorbed:

$$\Delta\epsilon = Q_v, \tag{34}$$

so that the energy can be regarded as the heat function at constant volume.

Various names have been given to the thermodynamic functions ψ, ζ, χ. Clerk Maxwell called ψ the available energy, but a certain amount of confusion has arisen because Helmholtz in 1882* used the term, free energy, for the same quantity. G. N. Lewis,† in his system of thermodynamics, has made use of the functions A, F and H which are identical with Gibbs's ψ, ζ, χ and has used the names:

A or ψ: Available energy.
F or ζ: Free energy.
H or χ: Heat content.

F. Massieu‡ was the first to show that the thermodynamical properties of a fluid of invariable composition may be deduced from a single function, which he called the characteristic function of the fluid. He made use of two such functions; which, in Gibbs' notation, are as follows:

$$\text{(1)} \qquad \frac{-\epsilon + t\eta}{t} = -\frac{\psi}{t},$$

$$\text{(2)} \qquad \frac{-\epsilon + t\eta - pv}{t} = -\frac{\zeta}{t}.$$

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* *Sitzungsber. preuss. Akad. Wiss*, **1**, 22 (1882).

† Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances* (1923).

‡ *Comptes rendus*, **69**, 858 and 1057, (1869).

Planck has also made use of the second function, which has the same properties in a system at constant temperature and pressure as the entropy at constant energy and volume.

8. Differentials of ϵ, ψ *and* ζ. The variations with temperature and pressure of the quantities ψ and ζ, for a homogeneous body of fixed composition, are obtained by differentiating (14) and (15) and comparing with (3). Thus

$$d\psi = d\epsilon - td\eta - \eta dt, \tag{35}$$

but since

$$d\epsilon = td\eta - pdv,$$

we have

$$d\psi = -pdv - \eta dt, \tag{36}$$

and

$$\left(\frac{d\psi}{dv}\right)_t = -p, \quad \left(\frac{d\psi}{dt}\right)_v = -\eta. \tag{37}$$

Similarly,

$$\begin{aligned} d\zeta &= d\epsilon - td\eta - \eta dt + pdv + vdp \\ &= -\eta dt + vdp; \end{aligned} \tag{38}$$

so that

$$\left(\frac{d\zeta}{dt}\right)_p = -\eta, \quad \left(\frac{d\zeta}{dp}\right)_t = v. \tag{39}$$

Now, if the system is heterogeneous, the quantity of matter in some of its parts may increase at the expense of that in other parts and we shall need to express the effect of such variations on the energy and on the quantities ψ, ζ and χ. Consider a single homogeneous mass containing the quantities m_1, m_2, $m_3, \ldots m_n$ of substances S_1, S_2, $S_3, \ldots S_n$. It is usually possible to express the composition of a mass in a number of different ways. It is immaterial which way is chosen, provided that the components are such that every possible independent variation in the composition of the mass can be expressed in terms of them. For example, possible variations in the composition of a solution of sulphuric acid in water may equally well be expressed by taking sulphuric acid and water, or sulphur trioxide and water, as components, but sulphur, oxygen and hydrogen are not admissible as components as their amounts cannot be independently varied. The change in the value of ζ of this mass when the amounts of $S_1, S_2, \ldots S_n$ are increased by $dm_1, dm_2, \ldots dm_n$, the temperature and pressure remaining constant, is given by

$$d\zeta = \left(\frac{d\zeta}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}} \cdot dm_1 + \left(\frac{d\zeta}{dm_2}\right)_{t,\,p,\,m_1,\,m_3,\,\text{etc.}} \cdot dm_2 \ldots + \left(\frac{d\zeta}{dm_n}\right)_{t,\,p,\,m_1,\,\ldots\,m_{n-1}} \cdot dm_n, \qquad (40)$$

and we may write

$$\left.\begin{aligned} \left(\frac{d\zeta}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}} &= \mu_1, \\ \left(\frac{d\zeta}{dm_2}\right)_{t,\,p,\,m_1,\,m_3,\,\text{etc.}} &= \mu_2, \text{ etc.,} \end{aligned}\right\} \qquad (41)$$

so that

$$(d\zeta)_{t,\,p} = \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n. \qquad (42)$$

When the temperature and pressure also vary, by combining with (38), we have

$$d\zeta = -\eta dt + vdp + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n, \qquad (43)\ [92]$$

whence, by (38),

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n, \qquad (44)\ [86]$$

and by (35)

$$d\psi = -\eta dt - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n. \qquad (45)\ [88]$$

The definition of μ_1, etc., given above, corresponds to the most familiar condition, viz., that of constant temperature and pressure. Since ζ is the free energy of the homogeneous mass, the quantity

$$\left(\frac{d\zeta}{dm_1}\right)_{t,\,p,\,m_2,\,\ldots\,m_n} = \mu_1$$

represents the rate of increase of ζ with the quantity of the component S_1, when the temperature, pressure and quantities of the other components remain constant. It is therefore the *partial free energy* of the first component. According to equations (44) and (45), μ_1 is also given by

$$\mu_1 = \left(\frac{d\epsilon}{dm_1}\right)_{\eta,\, v,\, m_2,\, \ldots\, m_n}, \qquad (46)\ [104]$$

and by

$$\mu_1 = \left(\frac{d\psi}{dm_1}\right)_{t,\, v,\, m_2,\, \ldots\, m_n}, \qquad (47)\ [104]$$

i.e. μ_1 is equal to the rate of change of ϵ with m_1, when the entropy, volume and quantities of the other components remain constant, and to the rate of change of ψ with m_1, when the temperature, volume and quantities of the other components remain constant.

Now all the terms in (44) are of the same kind, that is multiples of quantities (t, p, μ_1, etc.) which depend on the state of the system, by the differentials of quantities (η, v, m_1, etc.) which are directly proportional to the amount of matter in the state considered. We may therefore integrate (44) directly, obtaining:

$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n, \qquad (48)\ [93]$$

whence by (14), (15) and (16):

$$\psi = -pv + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n, \qquad (49)\ [94]$$

$$\zeta = \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n, \qquad (50)\ [96]$$

$$\chi = t\eta + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n. \qquad (51)\ [95]$$

A concrete picture of the process involved in this integration may be obtained as follows. If we take a homogeneous mass having entropy η and volume v, and containing quantities m_1, $m_2, \ldots m_n$ of the components S_1, $S_2, \ldots S_n$, and add quantities of a mass of the same composition and in the same state; t, p, μ_1, μ_2, etc., all remain unchanged and (44) may be applied to a finite addition:

$$\Delta\epsilon = t\Delta\eta - p\Delta v + \mu_1\Delta m_1 + \mu_2\Delta m_2 \ldots + \mu_n\Delta m_n\,,$$

where $\Delta\eta$, Δv, Δm_1, etc., are all proportional to the values of η, v, m_1, etc. in the original mass. We may thus continue these additions until we have doubled the amount of the original mass. Then, since $\Delta\eta = \eta$, $\Delta v = v$, $\Delta m_1 = m_1$, etc., the energy of the added substance is

$$\Delta\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n\,,$$

and this must be equal to the energy ϵ, of the mass originally present.

The general justification of this treatment depends on Euler's theorem on homogeneous functions. According to this theorem, if $y = \phi(x_1, x_2, \ldots x_n)$ be a homogeneous function of x_1, $x_2, \ldots x_n$ of the mth degree;

$$x_1 \frac{\partial y}{\partial x_1} + x_2 \frac{\partial y}{\partial x_2} \ldots + x_n \frac{\partial y}{\partial x_n} = my. \tag{52}$$

Now a homogeneous function of the mth degree is one for which

$$\phi(kx_1, kx_2, \ldots kx_n) = k^m\phi(x_1, x_2, \ldots x_n),$$

i.e., if each variable x_1, $x_2, \ldots x_n$ is multiplied by a quantity k, the value of the function is multiplied by k^m. The energy of a homogeneous mass is evidently a homogeneous function of the first degree with respect to η, v, m_1, $m_2, \ldots m_n$. If we increase each of these quantities k times, i.e., by taking k times as much of the homogeneous substance, the energy is increased in the same proportion. Therefore by Euler's theorem, putting $\epsilon = \phi(\eta, v, m_1, \ldots m_n)$ we have

$$\epsilon = \eta \frac{\partial\epsilon}{\partial\eta} + v \frac{\partial\epsilon}{\partial v} + m_1 \frac{\partial\epsilon}{\partial m_1} \ldots + m_n \frac{\partial\epsilon}{\partial m_n},$$

or

$$\epsilon = \eta t - vp + m_1\mu_1 \ldots + m_n\mu_n,$$

since

$$\left.\begin{aligned}\left(\frac{d\epsilon}{d\eta}\right)_{v,\, m_1 \,\ldots\, m_n} &= t,\\ \left(\frac{d\epsilon}{dv}\right)_{\eta,\, m_1 \,\ldots\, m_n} &= -\,p,\\ \left(\frac{d\epsilon}{dm_1}\right)_{\eta,\, v,\, m_2 \,\ldots\, m_n} &= \mu_1, \text{ etc.}\end{aligned}\right\} \tag{53}$$

Euler's theorem further states that if $\epsilon = \phi(\eta, v, m_1, m_2, \ldots m_n)$ is a homogeneous function of the first degree

$$\frac{\partial \epsilon}{\partial \eta} = t, \qquad \frac{\partial \epsilon}{\partial v} = -\,p, \qquad \frac{\partial \epsilon}{\partial m_1} = \mu_1, \text{ etc.,}$$

are functions of zero degree. Therefore, applying Euler's theorem to one of these functions, e.g. to $\partial\epsilon/\partial m_1$, we have:

$$\eta \frac{\partial^2 \epsilon}{\partial m_1 \cdot \partial \eta} + v \frac{\partial^2 \epsilon}{\partial m_1 \cdot \partial v} + m_1 \frac{\partial^2 \epsilon}{\partial {m_1}^2} + m_2 \frac{\partial^2 \epsilon}{\partial m_1 \cdot \partial m_2} \ldots + m_n \frac{\partial^2 \epsilon}{\partial m_1 \cdot \partial m_n} = 0, \tag{54}$$

or

$$\eta \frac{\partial t}{\partial m_1} - v \frac{\partial p}{\partial m_1} + m_1 \frac{\partial \mu_1}{\partial m_1} + m_2 \frac{\partial \mu_2}{\partial m_1} \ldots + m_n \frac{\partial \mu_n}{\partial m_1} = 0. \tag{55}$$

Therefore, in general,

$$\eta dt - vdp + m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n = 0. \quad (56)\ [97]$$

Gibbs obtains this equation by differentiating (48) in the most general manner, viz.,

$$d\epsilon = td\eta + \eta dt - pdv - vdp + \mu_1 dm_1 + m_1 d\mu_1 \ldots + \mu_n dm_n + m_n d\mu_n,$$

and comparing the result with (44), which is a complete differential.

Equation (56) provides a relation between the variations of the $n + 2$ quantities, t, p, $\mu_1, \ldots \mu_n$, which define the state of a homogeneous mass. If the variations of $n + 1$ of these quantities are given any arbitrary values, the variation of the remaining quantity can be determined by (56). A single homogeneous mass is therefore capable of only $n + 1$ independent variations of state.

Additional Relations

It will be convenient to give here some additional relations which are easily obtained from the equations of the last section. By (37) or (45) we have, for a body of fixed composition and mass (indicated by the subscript m),

$$t\left(\frac{d\psi}{dt}\right)_{v,\,m} = -\eta t, \tag{57}$$

or

$$t\left(\frac{d\psi}{dt}\right)_{v,\,m} = \psi - \epsilon. \tag{58}$$

This equation, which has been found a very convenient expression of the relation between ψ and ϵ, was first given explicitly by Helmholtz* and is known as the Gibbs-Helmholtz equation. An equivalent equation between ζ and χ is obtained from (39) or (43), viz:

$$t\left(\frac{d\zeta}{dt}\right)_{p,\,m} = -\eta t = \zeta - \chi. \tag{59}$$

Further, since

$$t^2\,\frac{d\,(\psi/t)}{dt} = t\,\frac{d\psi}{dt} - \psi,$$

we may write (58) as

$$\left(\frac{d(\psi/t)}{dt}\right)_{v,\,m} = -\frac{\epsilon}{t^2}, \tag{60}$$

and similarly (59) becomes

$$\left(\frac{d(\zeta/t)}{dt}\right)_{p,\,m} = -\frac{\chi}{t^2}\,. \tag{61}$$

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* *Sitzungsber preuss. Akad. Wiss.*, **1**, 22 (1882); *cf.* Gibbs, I, 412.

IV. The Conditions of Equilibrium between Initially Existent Parts of a Heterogenous System*

9. General Remarks. Gibbs first considers the equilibrium of heterogeneous systems when uninfluenced by gravity, by external electric forces, by distortion of the solid bodies, or by the effects of surface tension. A mass of matter of various kinds, the conditions of equilibrium of which are to be determined, is supposed to be "enclosed in a rigid and fixed envelop, which is impermeable to and unalterable by any of the substances enclosed, and perfectly non-conducting to heat." It is supposed that there are no non-isotropic strains in the solid bodies, and that the variations of energy and entropy which depend on the surfaces separating the heterogeneous mass are so small in comparison with those which depend on the masses themselves that they may be neglected. The effects excluded here are examined in detail in later parts of the Memoir.

Gibbs points out that "the supposition of a rigid and non-conducting envelop enclosing the mass under discussion involves no real loss of generality, for if any mass of matter is in equilibrium, it would also be so, if the whole or any part of it were enclosed in an envelop as supposed; therefore the conditions of equilibrium for a mass thus enclosed are the general conditions which must always be satisfied in case of equilibrium." The use of such an envelop ensures that the volume of the system remains constant and that no heat is received from or given up to any outside bodies. Since a system which is in equilibrium cannot undergo any irreversible change, its entropy must, under these conditions, remain constant.

In the first place, the conditions relating to the equilibrium between initially existing homogeneous parts of the mass are examined; the conditions for the formation of masses unlike any previously existing are discussed in a later section.

10. Conditions of Equilibrium When the Component Substances Are Independent of Each Other.† Let the energies of the separate homogeneous parts of the system be ϵ', ϵ'' etc.

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* Gibbs, I, 62–70.

† Gibbs, I, 62–67.

According to (44), the variation of the energy of the first homogeneous part through a change of entropy, or of volume, or by a change of its mass, is

$$d\epsilon' = t'd\eta' - p'dv' + \mu_1'dm_1' + \mu_2'dm_2' \ldots + \mu_n'dm_n'. \quad (62)$$

We will first suppose that the components $S_1, S_2, \ldots S_n$ are chosen so that $dm_1', dm_2', \ldots dm_n'$ are independent and express every possible variation in the composition of the homogeneous mass considered. With regard to this choice of components, we may note that if dm_1, dm_2 etc. are all independent, the number of components is evidently the *minimum* by which every possible variation can be expressed. Further, some of the terms in (62) may refer to substances which are not present in the mass considered, but are present in other parts of the system. If a component S_a is present in the homogeneous mass considered, so that its quantity m_a may be either increased or decreased, it is termed an *actual component* of the given mass. But if a component S_b is present in other parts of the system, but not in the homogeneous mass considered, so that it is a possibility that its quantity m_b can be increased but not decreased, it is termed a *possible component* of the given mass.

We will first consider the case in which each of the component substances $S_1, S_2, \ldots S_n$ is an actual component of each part of the system. The condition of equilibrium of the matter enclosed in the envelop, since its entropy cannot vary, is that its energy cannot decrease in any possible variation. Thus if $\delta\epsilon', \delta\epsilon''$, etc. represent the change of energy of different parts of the system in a variation of the state of the system, the condition of equilibrium is

$$\delta\epsilon' + \delta\epsilon'' + \delta\epsilon''' + \text{etc.} \geqq 0 \qquad (63)\ [14]$$

for all possible variations. Writing out the values of these variations in full, we have:

$$\begin{aligned} &t'\,\delta\eta' - p'\,\delta v' + \mu_1'\,\delta m_1' + \mu_2'\,\delta m_2' \ldots + \mu_n'\delta m_n' \\ &+t''\delta\eta'' - p''\delta v'' + \mu_1''\delta m_1'' + \mu_2''\delta m_2'' \ldots + \mu_n''\delta m_n'' \\ &+ \text{etc.} \geqq 0 \end{aligned} \qquad (64)\ [15]$$

for all possible variations which do not conflict with the conditions imposed or necessitated by the nature of the case. These conditions may be expressed in the following equations, which are termed the *equations of condition.*

(1) The entropy of the whole system is constant; or

$$\delta\eta' + \delta\eta'' + \delta\eta''' + \text{etc.} = 0, \qquad (65)\ [16]$$

(2) The volume of the whole system is constant; or

$$\delta v' + \delta v'' + \delta v''' + \text{etc.} = 0, \qquad (66)\ [17]$$

(3) The total mass of each component is constant; or

$$\left.\begin{aligned} \delta m_1' + \delta m_1'' + \delta m_1''' + \text{etc.} &= 0, \\ \delta m_2' + \delta m_2'' + \delta m_2''' + \text{etc.} &= 0, \\ \dots\dots\dots\dots\dots\dots\dots\dots \\ \delta m_n' + \delta m_n'' + \delta m_n''' + \text{etc.} &= 0. \end{aligned}\right\} \qquad (67)\ [18]$$

Now since all the quantities like $\delta\eta'$, $\delta v'$, $\delta m_1', \dots \delta m_n'$ may be either positive or negative, the left-hand side of (64) is only incapable of having negative values when (65), (66) and (67) are satisfied, if

$$t' = t'' = t''' = \text{etc.} \qquad (68)\ [19]$$

$$p' = p'' = p''' = \text{etc.} \qquad (69)\ [20]$$

$$\left.\begin{aligned} \mu_1' = \mu_1'' = \mu_1''' &= \text{etc.} \\ \mu_2' = \mu_2'' = \mu_2''' &= \text{etc.} \\ \dots\dots\dots\dots\dots\dots \\ \mu_n' = \mu_n'' = \mu_n''' &= \text{etc.} \end{aligned}\right\} \qquad (70)\ [21]$$

For example, consider the terms $\mu_1'\delta m_1' + \mu_1''\delta m_1'' + \mu_1'''\delta m_1''' + \text{etc.}$ Since

$$\delta m_1' + \delta m_1'' + \delta m_1''' + \text{etc.} = 0, \qquad (71)$$

it follows that

$$\mu_1'\delta m_1' + \mu_1''\delta m_1'' + \mu_1'''\delta m_1''' + \text{etc.} = 0$$

if $\mu_1' = \mu_1'' = \mu_1'''$, etc. But if μ_1'' were greater than μ_1', μ_1''', etc., there would be variations of the state of the system (if μ_1'' is positive, those for which $\delta m_1''$ is positive) which satisfy (71), but for which

$$\mu_1'\delta m_1' + \mu_1''\delta m_1'' + \mu_1'''\delta m_1''' + \text{etc.} > 0.$$

But since the quantities $\delta m_1'$, $\delta m_1''$, etc., may be both positive and negative, there are similar variations in which all these quantities have the opposite sign and for which

$$\mu_1'\delta m_1' + \mu_1''\delta m_1'' + \mu_1'''\delta m_1''' + \text{etc.} < 0.$$

The same considerations apply to the other sets of terms of the types $t\delta\eta$, $p\delta v$, $\mu_2\delta m_2$, etc., so that we may conclude that if (64) holds for all possible variations which satisfy (65), (66) and (67), the equalities (68), (69) and (70) must be satisfied.

Equations (68) and (69) express the conditions of thermal and mechanical equilibrium, viz., that the temperature and pressure must be constant throughout the system. Equations (70), which state that the value of μ for every component must be constant throughout the system, are "the conditions characteristic of chemical equilibrium." Gibbs calls the quantities μ_1, μ_2, etc., the *potentials* of the substances S_1, S_2, etc., and expresses the conditions (70) in the following statement: "*The potential for each component substance must be constant throughout the whole mass.*"

We will now consider the case in which one or more of the substances $S_1, S_2, \ldots S_n$ are only possible components of some parts of the system. Let S_2 be a possible component of that part of the system distinguished by (″). Then $\delta m_2''$ cannot have a negative value, so that equation (64) does not require that μ_2'' shall be equal to the value of μ_2 for those parts of the system of which S_2 is an actual component, but only that it shall not be less than that value. For if μ_2'' were greater than μ_2', μ_2''', etc., the sum of the terms

$$\mu_2'\delta m_2' + \mu_2''\delta m_2'' + \mu_2'''\delta m_2''' + \text{etc.}$$

would be positive if $\delta m_2''$ were positive, but since $\delta m_2''$ cannot be negative, this expression can never have a negative value. The condition of equilibrium (64) is therefore satisfied.

In this case, Gibbs therefore writes the conditions of equilibrium (70) in the following way:

$$\left.\begin{array}{l} \text{“}\mu_1 = M_1 \\ \text{for all parts of which } S_1 \text{ is an actual component, and} \\ \mu_1 \geqq M_1 \\ \text{for all parts of which } S_1 \text{ is a possible (but not actual)} \\ \text{component,} \\ \mu_2 = M_2 \\ \text{for all parts of which } S_2 \text{ is an actual component, and} \\ \mu_2 \geqq M_2 \\ \text{for all parts of which } S_2 \text{ is a possible (but not actual)} \\ \text{component,} \\ \text{etc.,} \end{array}\right\} \quad (72)\ [22]$$

M_1, M_2, etc., denoting constants, the value of which is only determined by these equations."

When a component is neither an actual nor a possible component of some part of the system, the terms $\mu\delta m$ and δm, which refer to this component in that part of the system of which it is neither an actual nor a possible component are absent from (64), and from the equations of condition (67). The conditions of equilibrium are otherwise unaffected. "Whenever, therefore, each of the different homogeneous parts of the given mass may be regarded as composed of some or of all of the same set of substances, no one of which can be formed out of the others, the condition which (with equality of temperature and pressure) is necessary and sufficient for equilibrium between the different parts of the given mass may be expressed as follows:—

The potential for each of the component substances must have a constant value in all parts of the given mass of which that substance is an actual component, and have a value not less than this in all parts of which it is a possible component."

11. Conditions of Equilibrium When Some Components Can

*Be Formed Out of others.** If the substances $S_1, S_2, \ldots S_n$ are not all independent of each other, i.e., if some of them can be formed out of others, the number of components is no longer the minimum number in terms of which every possible variation of the state of the system can be expressed. For example, if the system contains a solution of sodium chloride in water in equilibrium with the solid hydrate, $NaCl \cdot H_2O$, it may be convenient to regard the hydrate as a component, as well as sodium chloride and water. Every independent variation of the system can be expressed in terms of the two components sodium chloride and water, but these two components are not independently variable in the solid hydrate. Their ratio is fixed.

Consider a system containing, in addition to other substances, water, sodium chloride and the solid hydrate $NaCl \cdot H_2O$, and let the components S_1, S_2 and S_3 be water, sodium chloride and the hydrate respectively. We will suppose that the other components $S_4, \ldots S_n$ are independent of each other. The general condition of equilibrium, which may be written more briefly in the form

$$\Sigma t\delta\eta - \Sigma p\delta v + \Sigma\mu_1\delta m_1 + \Sigma\mu_2\delta m_2 \ldots + \Sigma\mu_n\delta m_n \geqq 0 \qquad (73)\ [23]$$

still holds, but the equations of condition

$$\Sigma\delta m_1 = 0, \qquad \Sigma\delta m_2 = 0, \qquad \Sigma\delta m_3 = 0, \qquad (74)\ [24]$$

do not necessarily hold, since the total amount of water and sodium chloride in the system may decrease and the total amount of the hydrate may increase. It is therefore necessary to replace (74) by equations representing the relation between the quantities of these substances. Thus, if b grams of sodium chloride combine with a grams of water to form $(a + b)$ grams of the hydrate, the quantity (δm_3) of the hydrate contains $\frac{a}{a+b}(\delta m_3)$ of water, and for the constancy of the actual total amount of water in the system (i.e., the sum of the amount of the component water and the amount of water contained in the component, hydrate), the equation

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* Gibbs, I, p. 67, line 24; p. 70, line 9.

$$\Sigma\delta m_1 + \frac{a}{a+b}\Sigma\delta m_3 = 0 \qquad (75)\ [25]$$

must hold.

Similarly the equation

$$\Sigma\delta m_2 + \frac{b}{a+b}\Sigma\delta m_3 = 0 \qquad (76)\ [25]$$

expresses the constancy of the sum of the amount of the component sodium chloride and the amount of sodium chloride present in the hydrate. The other equations of condition,

$$\Sigma\delta\eta = 0, \qquad \Sigma\delta v = 0, \qquad \Sigma\delta m_4 = 0, \qquad \text{etc.} \qquad (77)\ [26]$$

will remain unchanged.

We may first consider variations of the system which satisfy (74). Such variations evidently satisfy (75) and (76) and constitute some, but not all of the variations of which the system is capable. Equation (73) must hold for such variations, so that all the conditions of equilibrium, (68), (69) and (72) must apply to this case also. Therefore in (73), μ_1, μ_2, μ_3 have constant values M_1, M_2, M_3 in all parts of the system of which S_1, S_2 and S_3 are actual components. In the general case, when these conditions are satisfied (73) reduces to

$$M_1\Sigma\delta m_1 + M_2\Sigma\delta m_2 + M_3\Sigma\delta m_3 \geqq 0^*. \qquad (78)\ [27]$$

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* The proof of the equivalence of (78) with (73), given by Gibbs, may be stated as follows. When conditions (68), (69) and (72) are satisfied, and so long as δm is zero for every substance in all parts of the system of which that substance is not an actual component, i.e., for all terms in (73) involving a value of μ which may be greater than the corresponding value of M, we may write (73) in the form

$$t\Sigma\delta\eta - p\Sigma\delta v + M_1\Sigma\delta m_1 + M_2\Sigma\delta m_2 + M_3\Sigma\delta m_3 + M_4\Sigma\delta m_4 \ldots + M_n\Sigma\delta m_n \geqq 0,$$

and since

$$\Sigma\delta\eta = 0, \qquad \Sigma\delta v = 0, \qquad \Sigma\delta m_4 = 0, \qquad \text{etc.,}$$

We may eliminate $\Sigma\delta m_1$ and $\Sigma\delta m_2$ from this equation, by means of the equations of condition (75) and (76), so that it becomes

$$-aM_1\Sigma\delta m_3 - bM_2\Sigma\delta m_3 + (a+b)M_3\Sigma\delta m_3 \geqq 0, \qquad (79)\,[28]$$

so that, as $\Sigma\delta m_3$ may be either positive or negative,

$$-aM_1 - bM_2 + (a+b)M_3 = 0,$$

or

$$aM_1 + bM_2 = (a+b)M_3. \qquad (80)\,[29]$$

The relation between the values of the potentials, each of which is determined in a part of the system of which the substance concerned is an actual component, is thus:

$$a\mu_1 + b\mu_2 = (a+b)\mu_3. \qquad (81)$$

In a more general case, suppose that the system may be considered as having n components $S_1, S_2, \ldots S_n$, of which S_k, S_l, etc. can be formed out of the components S_a, S_b, etc., according to the equation:

$$\alpha\mathfrak{S}_a + \beta\mathfrak{S}_b + \text{etc.} = \kappa\mathfrak{S}_k + \lambda\mathfrak{S}_l + \text{etc.}, \qquad (82)\,[30]$$

where $\mathfrak{S}_a$, $\mathfrak{S}_b$, $\mathfrak{S}_k$, $\mathfrak{S}_l$, etc., denote the units of mass of the substances S_a, S_b, S_k, S_l, etc., and α, β, κ, λ, etc., the numbers of these units which enter into the relation. Then, as before, (73) will reduce to

$$M_a\Sigma\delta m_a + M_b\Sigma\delta m_b + \text{etc.} \ldots + M_k\Sigma\delta m_k$$
$$+ M_l\Sigma\delta m_l + \text{etc.} \geqq 0. \qquad (83)\,[31]$$

It is evidently possible to give $\Sigma\delta m_a$, $\Sigma\delta m_b$, $\Sigma\delta m_k$, $\Sigma\delta m_l$, etc., values proportional to α, β, $-\kappa$, $-\lambda$, etc., and also to the same

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this reduces to

$$M_1\Sigma\delta m_1 + M_2\Sigma\delta m_2 + M_3\Sigma\delta m_3 \geqq 0. \qquad (78)$$

The limitation of values of δm to zero, whenever they refer to parts of which the component in question is not an actual component, does not affect the range of possible values of $\Sigma\delta m_1$, $\Sigma\delta m_2$ and $\Sigma\delta m_3$ and may be disregarded.

values taken negatively; therefore

$$\alpha M_a + \beta M_b + \text{etc.} \ldots - \kappa M_k - \lambda M_l - \text{etc.} \ldots = 0,$$

or,

$$\alpha M_a + \beta M_b + \text{etc.} \ldots = \kappa M_k + \lambda M_l + \text{etc.} \ldots \quad (84)\ [33]$$

The relation between the quantities M_a, M_b, etc., is thus of the same form as that between the units of the component substances (82). These relations take a very simple form if we employ as the unit quantity of each substance, its formula-weight in grams. Thus if we take as unit quantities of water, sodium chloride and the hydrate, $NaCl \cdot H_2O$ the quantities in grams represented by the symbols H_2O, $NaCl$ and $NaCl \cdot H_2O$, the relation between these substances is represented qualitatively and quantitatively by the equation.

$$H_2O + NaCl = NaCl \cdot H_2O.$$

With this choice of units, (84) becomes

$$M_{H_2O} + M_{NaCl} = M_{NaCl \cdot H_2O}.$$

Therefore the values of μ_{H_2O}, μ_{NaCl} and $\mu_{NaCl \cdot H_2O}$ for these substances, in parts of the system of which they are present as actual components, are related by the equation

$$\mu_{H_2O} + \mu_{NaCl} = \mu_{NaCl \cdot H_2O}.$$

Similarly, if the substances hydrogen chloride, oxygen, water and chlorine are components of a system when the unit of quantity of each substance is the quantity (in grams) represented by its chemical formula (82) becomes

$$2HCl + \tfrac{1}{2}O_2 = H_2O + Cl_2,$$

and equation (84) takes the form

$$2M_{HCl} + \tfrac{1}{2}M_{O_2} = M_{H_2O} + M_{Cl_2}.$$

Thus the values of μ in parts of the system of which these substances are present as actual components, are related by the equation

$$2\mu_{HCl} + \tfrac{1}{2}\mu_{O_2} = \mu_{H_2O} + \mu_{Cl_2},$$

and this is evidently the relation between the μ's in a gaseous mass containing all four components. In this case we may observe that if the gram were taken as the unit mass of all four substances, the relation between the components would be (approximately)

$$73\ \mathfrak{S}_a + 16\ \mathfrak{S}_b = 18\ \mathfrak{S}_k + 71\ \mathfrak{S}_l,$$

where $\mathfrak{S}_a$, $\mathfrak{S}_b$, $\mathfrak{S}_k$, $\mathfrak{S}_l$ represent one gram of hydrogen chloride, oxygen, water and chlorine, respectively; and (84) would take the form

$$73\ M_a + 16\ M_b = 18\ M_k + 71\ M_l;$$

or,

$$73\ \mu_a + 16\ \mu_b = 18\ \mu_k + 71\ \mu_l,$$

where the value of μ for each substance is that in a part of the system in which it is present as an actual component.

Again, the four substances magnesium chloride, potassium sulphate, magnesium sulphate, potassium chloride, may be regarded as components of a solution made by dissolving magnesium chloride and potassium sulphate in water, since the last two may be formed out of the first two according to the equation

$$MgCl_2 + K_2SO_4 = MgSO_4 + 2KCl.$$

If the units of quantity of the four substances are the quantities represented by the symbols $MgCl_2$, K_2SO_4, $MgSO_4$ and KCl, (84) takes the form

$$M_{MgCl_2} + M_{K_2SO_4} = M_{MgSO_4} + 2\,M_{KCl},$$

so that the potentials in the solution are related by the equation

$$\mu_{MgCl_2} + \mu_{K_2SO_4} = \mu_{MgSO_4} + 2\,\mu_{KCl}.$$

Gibbs shows that if there are r independent relations similar to (82) between the components, S_1, $S_2, \ldots S_n$, r equations similar to (84) must be satisfied in addition to the general conditions (68), (69) and (72), provided that each of the components S_1, $S_2, \ldots S_n$ is an actual component of some part of the system.

But it must be understood that a relation between the components such as (82) implies not merely the chemical identity of the substances represented, but also that the change of the substances represented by the left hand member into the substances represented by the right hand member can occur in the system and is not prevented by passive resistances to change. For example, in a system containing water and free hydrogen and oxygen, at ordinary temperatures, the combination of hydrogen and oxygen to form water is prevented by "passive resistances to change," so that we cannot write

$$1\,\mathfrak{S}_{\mathrm{H}} + 8\,\mathfrak{S}_{\mathrm{O}} = 9\,\mathfrak{S}_{Aq}$$

as a relation between the components, for under these conditions there can be no change in the amounts of water in the system in any *possible* variation of its state. Water must therefore be treated as an independent component and there will be no necessary relation between the potential of water and the potentials of hydrogen and oxygen.

12. Effect of a Diaphragm (*Equilibrium of Osmotic Forces*).* Consider the equilibrium between two homogeneous fluids, separated by a diaphragm which is permeable to some of the components and impermeable to others. Suppose that the two fluids are enclosed in a rigid, heat-insulating envelop as before, but that they are separated by a rigid, immovable diaphragm. We shall distinguish quantities which refer to the two sides of the diaphragm by single and double accents.

As before, the total entropy of the system is constant, i.e.,

$$\delta\eta' + \delta\eta'' = 0, \qquad (85)\ [72]$$

and the total quantities in both fluids of those components,

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* Gibbs, I, 83–85.

S_h, S_i, etc., which can pass through the diaphragm, is constant, i.e.,

$$\delta m_h' + \delta m_h'' = 0, \qquad \delta m_i' + \delta m_i'' = 0, \text{ etc.,} \qquad (86)\ [75]$$

but the quantities of those components, S_a,S_b, etc., which cannot pass through the diaphragm must be constant in each fluid, i.e.,

$$\delta m_a' = 0, \quad \delta m_a'' = 0, \quad \delta m_b' = 0, \quad \delta m_b'' = 0, \text{ etc.,} \qquad (87)\ [74]$$

and the volume of the fluid mass on *each* side of the diaphragm must be constant, i.e.,

$$\delta v' = 0, \qquad \delta v'' = 0. \qquad (88)\ [73]$$

The general condition of equilibrium (64), which takes the form

$$\begin{aligned} t'\delta\eta' - p'\delta v' + \mu_a'\delta m_a' + \mu_b'\delta m_b' \ldots + \mu_h'\delta m_h' + \mu_i'\delta m_i' \ldots \\ + t''\delta\eta'' - p''\delta v'' + \mu_a''\delta m_a'' + \mu_b''\delta m_b'' \ldots \\ + \mu_h''\delta m_h'' + \mu_i''\delta m_i'' \ldots \geqq 0, \end{aligned}$$

will now give the following particular conditions:

$$(1) \qquad t' = t'', \qquad (89)\ [76]$$

$$(2) \qquad \mu_h' = \mu_h'', \qquad \mu_i' = \mu_i'', \qquad \text{etc.,} \qquad (90)\ [77]$$

if S_h, S_i, etc., are actual components of both fluids; but it is not necessary that

$$p' = p'', \qquad (91)$$

or

$$\mu_a' = \mu_a'', \qquad \mu_b' = \mu_b'', \qquad \text{etc.} \qquad (92)$$

Thus the values of the potentials of components which are present on both sides of the diaphragm and which can pass through it must be equal, but it is not necessary that the pressures, or the values of the potentials of those substances to which the diaphragm is impermeable, shall be the same in the two fluids.

Gibbs points out that these conditions do not depend on the supposition that the volume of each fluid mass is kept constant. The same conditions of equilibrium can easily be obtained, if we suppose the volumes variable. In this case the equilibrium must be preserved by external pressures P', P'' acting on the external surfaces of the fluids, equal to the internal hydrostatic pressures of the liquids p', p''. Suppose that external pressures P' and P'' are applied to the two fluids, which are separated by an immovable diaphragm, in some such arrangement as Figure 1. When the volume of the fluid (*I*) increases by $\delta v'$ work is done against the external pressure P' and the energy of the source of this pressure is increased by $P'\delta v'$. Similarly when the volume of fluid (*II*) is increased by $\delta v''$, the energy of the source of the pressure P'' is increased by $P''\delta v''$. These energy changes must be added to the energy change of the fluids in order to find the conditions of equilibrium. The general condition of equilibrium for constant entropy thus becomes

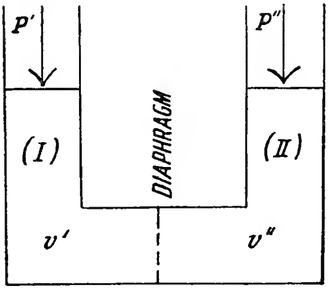

FIG. 1

$$\delta\epsilon' + \delta\epsilon'' + P'\delta v' + P''\delta v'' \geqq 0. \qquad (93)\ [79]$$

From this equation we can derive the same internal conditions of equilibrium as before, and in addition, the external conditions:

$$p' = P', \qquad p'' = P''.$$

When we have a pure solvent S_1 and a solution of a substance S_2 in S_1 separated by a membrane which is permeable to

S_1 only, it is necessary for equilibrium that $t' = t''$ and $\mu_1' = \mu_1''$, but not that $\mu_2' = \mu_2''$, or that $p' = p''$. The difference of hydrostatic pressure on the two sides of the membrane which is necessary to preserve equilibrium is the osmotic pressure of the solution, and is that which is required to make the value of potential of S_1 in the solution the same as its value in the solvent. We shall calculate its value in simple cases in a later section.

V. Coexistent Phases

13. The Phase Rule.[*] The variation of the energy of a homogeneous body, containing n independently variable components, has been expressed by the equation:

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n. \qquad (95)$$

In this equation, there are altogether $2n + 5$ variables, viz.,

$$m_1, m_2, \ldots m_n,$$
$$\mu_1, \mu_2, \ldots \mu_n,$$

and $$\epsilon, t, \eta, p, v.$$

These quantities are not all independent, for the $n + 2$ quantities, $t, p, \mu_1, \mu_2, \ldots \mu_n$ can be derived from the original equation by differentiation. Thus, the equations

$$\left(\frac{d\epsilon}{d\eta}\right)_{v, m_1, \ldots m_n} = t, \qquad \left(\frac{d\epsilon}{dv}\right)_{\eta, m_1, \ldots m_n} = -p,$$
$$\left(\frac{d\epsilon}{dm_1}\right)_{\eta, v, m_2, \ldots m_n} = \mu_1, \qquad \text{etc.}$$

give us $n + 2$ independent relations between the $2n + 5$ variables. The original equation (95) is an additional relation, so that if ϵ is known as a function of $\eta, v, m_1, \ldots m_n$, there are altogether $n + 3$ known relations between the $2n + 5$ variables and the remainder, $n + 2$ in number, are independent.

The homogeneous body may thus undergo $n + 2$ independent variations, e.g., the quantities $m_1, \ldots m_n$, η, v may be varied independently of each other. But if they are all varied in the same proportion, the result is a change in the *amount* of the body, while its state and composition remain unchanged. A variation of the *state* or *composition* of the body involves a change in at least one of the ratios of these quantities. There are $n + 1$ independent ratios of these $n + 2$ quantities (e.g., the ratios m_1/v, $m_2/v, \ldots m_n/v$, η/v) so that the number of independent variations of state and composition of a homogeneous body is $n + 1$.

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[*] Gibbs, I, 96–97.

Gibbs calls a variation of the thermodynamic state or composition of a body, as distinguished from a variation of its amount, a variation of the *phase* of the body. In a heterogeneous system, such bodies as differ in composition or state are regarded as different phases of the matter of the system, and all bodies which differ only in quantity or form as different examples of the same phase. Thus we may say that the number of independent variations of the phase of a homogeneous body which contains n independent components is $n + 1$.

Consider a system of r phases each of which has the same n independently variable components. The total number of independent variations of the r phases, considered separately, is $(n + 1)r$. When the r phases are coexistent these variations are subject to the conditions (68), (69) and (70), i.e., to $(r - 1)(n + 2)$ conditions. The number of independent variations of phase of which the system is capable is therefore

$$\mathfrak{F} = (n + 1)r - (n + 2)(r - 1) = n - r + 2. \qquad (96)$$

The integer $\mathfrak{F}$ has been called *the number of degrees of freedom* of the system.

This relation, which is now known as the *phase rule,* holds even if each phase has not the same n independently variable components. For if a component is a possible, but not an actual, component of some part of the system, the variation, δm, of its quantity in that part, can only be positive, whereas in the previous case it can be either positive or negative, and instead of the equality $\mu = M$, we have the condition $\mu \geqq M$. The number of independent variations of the system is therefore unaltered. When a component is neither an actual nor a possible component of some part of the system, the total number of variations of the phases, considered separately, is one less than $(n + 1)r$ and, since there is no condition as to the potential of this component in the part of the system of which it is not a possible component, the number of conditions is also reduced by one. Finally we may consider the case in which some of the components can be formed out of others. Let n, as before, be the number of independently variable components of the system as a whole, and let $n + h$ be the total number of substances which are regarded as components in various parts of the system. If all these latter components were independent, the number of degrees of freedom of the system would be $n + h - r + 2$. But, since they are not independent, there are h additional equations between their potentials similar to (84), corresponding to h equations representing the relations between the units of these substances. The number of independent variations of the system, therefore, is still $n - r + 2$.

Gibbs deduced the phase rule more concisely by the following considerations. "A system of r coexistent phases, each of which has the same n independently variable components is capable of $n + 2 - r$ variations of phase. For the temperature, the pressure, and the potentials for the actual components have the same values in the different phases, and the variations of these quantities are by [97] subject to as many conditions as there are different phases. Therefore, ... the number of independent variations of phase of the system, will be $n + 2 - r$.

"Or, when the r bodies considered have not the same independently variable components, if we still denote by n the number of independently variable components of the r bodies taken as a whole, the number of independent variations of phase of which the system is capable will still be $n + 2 - r$. In this case, it will be necessary to consider the potentials for more than n component substances. Let the number of these potentials be $n + h$. We shall have by [97], as before, r relations between the variations of the temperature, of the pressure, and of these $n + h$ potentials, and we shall also have . . . . h relations between these potentials, of the same form as the relations which subsist between the different component substances," (that is, the variations of the $n + h + 2$ quantities, viz., $n + h$ potentials, and temperature and pressure, are subject to $r + h$ relations).

We may illustrate the phase rule by reference to systems containing a single component ($n = 1$). If there is only one phase, $\mathfrak{F} = 2$, i.e., the temperature and the pressure may be varied independently. If there are two phases, e.g., liquid and vapor, only one independent variation of phase is possible, so that the temperature and the pressure cannot be varied independently of each other. A variation of the temperature involves a necessary variation of the pressure, if the two phases are to remain in equilibrium. If there are three phases of the substance, $\mathfrak{F} = 0$, i.e., it is impossible to vary either the temperature or the pressure while the three phases remain. The conditions under which three phases of the same substance can coexist are thus invariant. Gibbs remarks that "it seems not improbable that in the case of sulphur and some other substances there is more than one triad of coexistent phases" (a prediction which has been verified in numerous cases), "but it is entirely improbable that there are four coexistent phases of any simple substance."

*14. The Relation between Variations of Temperature and Pressure in a Univariant System.** According to (96), a system of $r = n + 1$ coexistent phases has one degree of freedom. The pressure and the temperature cannot therefore be varied independently and there must be a relation between a variation of the temperature and the consequent change of pressure.

We will first consider a system of one component in two phases, e.g., liquid and vapor. The variations of each phase must be in accordance with (56), so that we may write

$$\left.\begin{aligned} v'\,dp' &= \eta'\,dt' + m'\,d\mu', \\ v''dp'' &= \eta''dt'' + m''d\mu''. \end{aligned}\right\} \qquad (97)$$

If the two phases are to remain in equilibrium,

$$dp' = dp'', \qquad dt' = dt'', \qquad d\mu' = d\mu''.$$

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* Gibbs, I, 97–98.

Therefore, eliminating $d\mu'$ from (97), we have

$$(v'm'' - v''m')dp = (\eta'm'' - \eta''m')dt,$$

or

$$\frac{dp}{dt} = \frac{\eta'm'' - \eta''m'}{v'm'' - v''m'}. \qquad (98)\ [131]$$

If we consider unit quantity of the substance in each of the two phases, we may put $m' = 1$ and $m'' = 1$, so that (98) becomes

$$\frac{dp}{dt} = \frac{\eta' - \eta''}{v' - v''} = \frac{\eta'' - \eta'}{v'' - v'}.$$

Now,

$$\eta'' - \eta' = Q/t,$$

where Q is the heat absorbed when a unit of the substance passes from one state to the other, at the same temperature and pressure, and $v'' - v'$ is the corresponding change of volume. Thus, we obtain the Clapeyron-Clausius equation:[*]

$$\frac{dp}{dt} = \frac{Q}{t(v'' - v')}. \qquad (99)$$

Gibbs derives a general expression, similar to (98), for a system of n independently variable components, $S_1, \ldots S_n$, in $r = n + 1$ coexistent phases. In this case there are $n + 1$ equations of the general form of (56), one for each of the existent phases. But the values of dp and dt must be the same for all phases and the same is true of $d\mu_1$, $d\mu_2$, etc., so far as each of these occurs in the different equations. Thus, if each phase is regarded as being composed of some or all of the n independent components, a variation of the system must satisfy the following equations:

$$\left.\begin{aligned} v'\ dp &= \eta'\ dt + m_1'\ d\mu_1 + m_2'\ d\mu_2\ \ldots\ + m_n'\ d\mu_n,\\ v''\ dp &= \eta''\ dt + m_1''\ d\mu_1 + m_2''\ d\mu_2\ \ldots\ + m_n''\ d\mu_n,\\ v'''dp &= \eta'''dt + m_1'''d\mu_1 + m_2'''d\mu_2\ \ldots\ + m_n'''d\mu_n,\\ \text{etc.}& \end{aligned}\right\}(100)\ [127]$$

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[*] Clapeyron, *J. de l'école polytechnique*, Paris, **14**, 173, (1834). Clausius, *Ann. Physik*, **81**, 168, (1850). Also obtained by W. Thomson, *Phil. Mag.*, **37**, 123, (1850).

There are thus $n + 1$ linear equations between the $n + 2$ quantities dp, dt, $d\mu_1, \ldots d\mu_n$, by means of which the n quantities, $d\mu_1, d\mu_2, \ldots d\mu_n$ can be eliminated. We thus obtain, in the notation of determinants:

$$\begin{vmatrix} v' & m_1' & m_2' & \ldots m_n' \\ v'' & m_1'' & m_2'' & \ldots m_n'' \\ v''' & m_1''' & m_2''' & \ldots m_n''' \end{vmatrix} dp = \begin{vmatrix} \eta' & m_1' & m_2' & \ldots m_n' \\ \eta'' & m_1'' & m_2'' & \ldots m_n'' \\ \eta''' & m_1''' & m_2''' & \ldots m_n''' \end{vmatrix} dt. \quad (101)\ [129]$$

As a simple example, we shall work out the application of this equation to a system containing as separate phases, calcium carbonate, lime and carbon dioxide. The two components lime and carbon dioxide are sufficient to express every possible variation of the system. Let the entropies, volume and quantities of the phases be specified as follows.

	Gas phase	Solid phase (lime)	Solid phase (calcium carbonate)
Volume	v'	v''	v'''
Entropy	η'	η''	η'''
Quantity of carbon dioxide	m_1'	0	m_1'''
Quantity of lime	0	m_2''	m_2'''

where m_1''' and m_2''' are necessarily in the proportion $a : b$ in which lime and carbon dioxide unite to form calcium carbonate. Then, by (101), we have the following relation between variations of the temperature and the pressure:

$$\begin{vmatrix} v' & m_1' & 0 \\ v'' & 0 & m_2'' \\ v''' & m_1''' & m_2''' \end{vmatrix} dp = \begin{vmatrix} \eta' & m_1' & 0 \\ \eta'' & 0 & m_2'' \\ \eta''' & m_1''' & m_2''' \end{vmatrix} dt,$$

so that

$$\frac{dp}{dt} = \frac{\eta''' m_1' m_2'' - \eta' m_1''' m_2'' - \eta'' m_1' m_2'''}{v''' m_1' m_2'' - v' m_1''' m_2'' - v'' m_1' m_2'''}. \quad (102)$$

If the system consists of a quantity a of lime and b of carbon dioxide, together with a quantity $(a + b)$ of calcium carbonate, we shall have

$$m_1' = m_1''' = b, \text{ and } m_2'' = m_2''' = a,$$

and (102) reduces to

$$\frac{dp}{dt} = \frac{\eta''' - \eta' - \eta''}{v''' - v' - v''} = \frac{Q}{t.\Delta v}, \tag{103}$$

where Q is the heat absorbed when a quantity $a + b$ of calcium carbonate is dissociated into lime and carbon dioxide at the same temperature and pressure, and Δv is the increase of volume in the same change. For $\eta''' - \eta' - \eta''$ is the difference between the entropy of a quantity $(a + b)$ of calcium carbonate, and that of the quantities a of lime and b of carbon dioxide. $Q = t(\eta''' - \eta' - \eta'')$ is thus the heat absorbed in the dissociation of the calcium carbonate.

When the number of potentials considered in various parts of the system is $n + h$, there will be h independent relations between them, by means of which the variations of h of the potentials may be eliminated from the equations of the form of (100) in which they occur. We may thus obtain $n + 1$ equations between the n potentials of the independently variable components of the system as a whole.

*15. Cases in Which the Number of Degrees of Freedom is Greater Than One.** *(a) Systems of Two or More Components in Two Phases.* We will consider first the case of two independent components in two phases. We shall have two equations similar to (100), one for each phase:

$$v'\,dp = \eta'\,dt + m_1'\,d\mu_1 + m_2'\,d\mu_2,$$

$$v''dp = \eta''dt + m_1''d\mu_1 + m_2''d\mu_2. \tag{104}$$

Eliminating $d\mu_2$ from these equations, we obtain:

$$(v'm_2'' - v''m_2')dp = (\eta'm_2'' - \eta''m_2')dt + (m_1'm_2'' - m_1''m_2')d\mu_1, \tag{105}$$

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* Gibbs, I, 99–100.

i.e., the system can undergo two independent variations, in accordance with (96). Now if the proportions of the two components are the same in the two phases, i.e., if

$$\frac{m_1'}{m_2'} = \frac{m_1''}{m_2''},$$

the coefficient of $d\mu_1$ in (105) is zero, so that

$$(v'm_2'' - v''m_2')dp = (\eta'm_2'' - \eta''m_2')dt, \tag{106}$$

i.e., the same relation between dp and dt holds, as for a single component. For example, in the equilibrium between ammonium chloride and its vapor, the latter may contain ammonia and hydrogen chloride, formed by dissociation. These two substances may be regarded as the independently variable components of the system, but if no excess of either of them is added the ratios of their amounts are the same in both phases. Then (106) holds, so that the system behaves as if it had a single component.

When there are n independent components in the two phases, then in the absence of any restriction on their proportions the number of degrees of freedom is $\mathfrak{F} = n + 2 - 2 = n$. But when the quantities of all components are proportional in the two phases, the equality of the $n - 1$ ratios of $m_1', m_2', \ldots m_n'$ with the $n - 1$ ratios of $m_1'', m_2'', \ldots m_n''$ gives $n - 1$ additional conditions, so that the number of degrees of freedom is reduced to one and there is a relation similar to (106) between the variations of temperature and pressure.

Again, in a system of two components in two phases, at constant temperature, (105) becomes

$$\frac{dp}{d\mu_1} = \frac{m_1'\,m_2'' - m_1''\,m_2'}{v'\,m_2'' - v''\,m_2'}. \tag{107}$$

If the proportions of the two components are the same in the two phases, the numerator of the fraction on the right is zero, so that

$$\frac{dp}{d\mu_1} = 0.$$

Thus, at constant temperature, the pressure is in general a maximum or a minimum when the composition (i.e., the proportions of the two components) of the two phases is identical. Similarly, it can be shown that, at constant pressure, the temperature of the two coexistent phases is in general a maximum or a minimum when the composition of the two phases is identical.

Applying these relations to the equilibrium between a binary liquid and its vapor, we see that (1) at constant temperature the vapor pressure is a maximum or a minimum when the vapor has the same composition as the liquid, and (2) the temperature at which the two phases are in equilibrium at constant pressure, i.e., the boiling point, is a maximum or a minimum when the composition of the two phases is identical. These rules were arrived at independently by Konowalow.* As an example of this behavior, Figure 2 shows the boiling points and compositions of the liquid and vapor phases of ethyl alcohol and benzene.

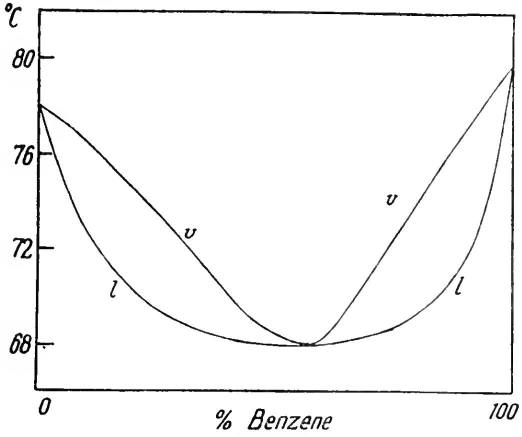

Fig. 2

Similarly, the temperature at which a binary liquid is in equilibrium with a solid phase, which may be a solid solution of the same components (mixed crystals) or a compound of invariable composition, is a maximum or a minimum, for constant pressure, when the two phases have the same composition. Examples of this behavior are shown in Figures

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* *Wied. Annalen*, **14**, 48, (1881).

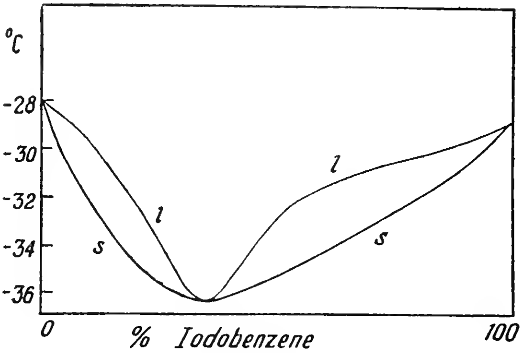

FIG. 3

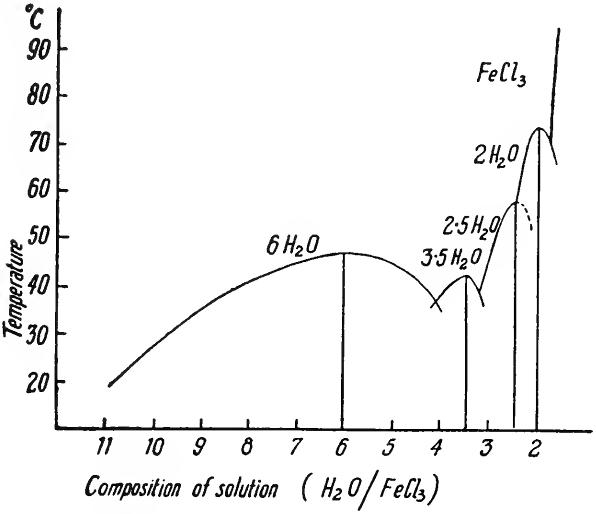

FIG. 4

3 and 4. Figure 3 shows the compositions of the solutions and mixed crystals of bromobenzene and iodobenzene which are in equilibrium with each other (at constant pressure) at different temperatures. The composition of the two phases is the same

when the temperature is a minimum. Figure 4 shows the conditions under which aqueous solutions of ferric chloride are in equilibrium with various solid compounds of the same components. A maximum in the temperature-composition curve occurs when the liquid phase has the same composition as the solid compound with which it is in equilibrium.*

(*b*) *Systems of Three Components in Three Coexistent Phases.* In this case, we have three equations similar to (100):

$$\left.\begin{aligned} v'\,dp &= \eta'\,dt + m_1'\,d\mu_1 + m_2'\,d\mu_2 + m_3'\,d\mu_3, \\ v''\,dp &= \eta''\,dt + m_1''\,d\mu_1 + m_2''\,d\mu_2 + m_3''\,d\mu_3, \\ v'''dp &= \eta'''dt + m_1'''d\mu_1 + m_2'''d\mu_2 + m_3'''d\mu_3, \end{aligned}\right\} \quad (108)$$

from which, by eliminating $d\mu_1$ and $d\mu_2$, we obtain:

$$\begin{vmatrix} v' & m_1' & m_2' \\ v'' & m_1'' & m_2'' \\ v''' & m_1''' & m_2''' \end{vmatrix} dp = \begin{vmatrix} \eta' & m_1' & m_2' \\ \eta'' & m_1'' & m_2'' \\ \eta''' & m_1''' & m_2''' \end{vmatrix} dt$$

$$+ \begin{vmatrix} m_1' & m_2' & m_3' \\ m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \end{vmatrix} d\mu_3. \qquad (109)\ [132]$$

When the composition of one of the three phases is such as can be produced by combining the other two, i.e., if we may take quantities of the three phases such that

$$\begin{aligned} m_1' &= m_1'' + m_1''', \\ m_2' &= m_2'' + m_2''', \\ m_3' &= m_3'' + m_3'''; \end{aligned}$$

the last of these determinants is zero, so that when $dt = 0$,

$$\frac{dp}{d\mu_3} = 0;$$

and when $dp = 0$,

$$\frac{dt}{d\mu_3} = 0.$$

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* A more exhaustive discussion of systems of two components in two phases is given on pages 175–177. Compare also Article H of this volume.

Since similar equations can be obtained for the other components, the pressure will thus in general be a maximum or a minimum at constant temperature, and the temperature a maximum or minimum at constant pressure when the foregoing condition is fulfilled.

For example, the three components water, alcohol, salt may give rise to a system of the three phases, solid, salt-solution, vapor. When the composition of the solution is such that it can be formed by combining quantities of the salt and the vapor, i.e., when the proportions of alcohol and water in the vapor are the same as in the solution, the pressure is a maximum or a minimum at constant temperature. Again, in the three component system; potassium sulphate, aluminium sulphate, water; with the three phases, viz., solid potassium alum, solution, vapor, the vapor pressure is a maximum or a minimum when the solution can be formed out of the solid salt and the vapor, i.e., when it contains the two salts in the same proportions as in the solid phase.

VI. Values of the Potentials in Very Dilute Solutions

*16. A Priori Considerations.** We may draw some conclusions as to the values of the potentials in a homogeneous mass, when the quantity of one of the components is very small, from the form of (56). Applying this equation to a homogeneous mass having two independently variable components, we obtain, when t, p and m_1 are constant

$$m_1 \left(\frac{d\mu_1}{dm_2}\right)_{t,\,p,\,m_1} + m_2 \left(\frac{d\mu_2}{dm_2}\right)_{t,\,p,\,m_1} = 0. \quad (110)\ [210]$$

When $m_2 = 0$, this equation requires that either

$$\left(\frac{d\mu_1}{dm_2}\right)_{t,\,p,\,m_1} = 0, \quad (111)\ [211]$$

or

$$\left(\frac{d\mu_2}{dm_2}\right)_{t,\,p,\,m_1} = \infty. \quad (112)\ [212]$$

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* Gibbs, I, 135–138.

We can distinguish between these possibilities by making use of a proposition which we shall obtain in a later section,* viz., that when t, p, and m_2 are constant, μ_1 is an increasing function of m_1. We shall now consider two cases.

(*a*) *m_2 Is Capable of Negative As Well As Positive Values.* Thus if we regard the hydrate $FeCl_3 \cdot 6H_2O$ (S_1) and anhydrous ferric chloride (S_2) as the components of a solution of ferric chloride and water, the amount of ferric chloride will be negative in solutions containing a smaller proportion of ferric chloride than the hydrate itself and positive in solutions containing a greater proportion. We may add the hydrate S_1 to solutions for which the amount of ferric chloride is either negative or positive. In both cases μ_1 is increased. Therefore μ_1 must be a maximum when the mass consists wholly of S_1, i.e., when $m_2 = 0$. Therefore, if m_2 is capable of negative as well as positive values,

$$\left(\frac{d\mu_1}{dm_2}\right)_{p,\,t,\,m_1} = 0, \tag{113}$$

when $m_2 = 0$.

(*b*) *m_2 Is Capable Only of Positive Values.* For example, if water (S_1) and ferric chloride (S_2) are regarded as the components of the solutions, m_2 cannot have negative values. The potential of water (μ_1) must increase when water is added to a ferric chloride solution, and therefore decrease when ferric chloride is added to the solution. Thus, in the limiting case when $m_2 = 0$, the value of the differential coefficient in (111) cannot be positive.

Gibbs points out that "if we consider the physical significance of this case, viz., that an increase of m_2 denotes an addition to the mass in question of a substance not before contained in it," there does not appear "any reason .... for supposing that this differential coefficient has generally the value zero." Suppose that we have a mass of water in equilibrium with ice. The addition of a salt to the water will destroy the possibility of this equilibrium at the same temperature and pressure and, if the temperature and pressure are kept constant, the liquid will dissolve the ice. Similarly the addition of a salt to water causes a decrease in the pressure of water vapor which is in equilibrium with the liquid at the same temperature. Both phenomena show "that μ_1 (the potential for water in the liquid mass) is diminished by the addition of the salt, when the temperature and pressure are maintained constant. Now there seems to be no *a priori* reason for supposing that the ratio of this diminution of the potential for water to the quantity of the salt which is added vanishes with this quantity. We should rather expect that, for small quantities of the salt, an effect of this kind would be proportional to its cause, i.e., that the differential coefficient in [211] would have a finite negative value for an infinitesimal value of m_2. That this is the case with respect to numerous watery solutions of salts is distinctly indicated by the experiments of Wüllner* on the tension of the vapor yielded by such solutions, and of Rüdorff† on the temperature at which ice is formed in them; and unless we have experimental evidence that cases are numerous in which the contrary is true, it seems not unreasonable to assume, as a *general* law, that when m_2 has the value zero and is incapable of negative values, the differential coefficient in [211] will have a finite negative value, and that equation [212] will therefore hold true." We may observe that the truth of this law has been confirmed by numerous more exact experimental investigations.

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* See page 167.

The change of μ_1 caused by the addition of a small amount dm_2 of S_2 is evidently inversely proportional to the amount (m_1) of S_1, so that we may write, in the limiting case, when $m_2 = 0$,

$$\left(\frac{d\mu_1}{dm_2}\right)_{t,\,p,\,m_1} = -\frac{A'}{m_1}, \tag{114}$$

where A' is positive and independent of m_1.
Then, by (110),

$$m_2\left(\frac{d\mu_2}{dm_2}\right)_{t,\,p,\,m_1} = A',$$

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* *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

† *Pogg. Ann.*, **114**, 63 (1861).

i.e.,

$$\left(\frac{d\mu_2}{d \log m_2}\right)_{t,\, p,\, m_1} = A'. \qquad (115)\ [214]$$

The integral of this equation may be put in the form

$$\mu_2 = A' \log \frac{Bm_2}{m_1}, \qquad (116)\ [215]$$

where B, like A', is independent of m_2 and m_1. This equation holds for such small values of m_2/m_1 that $d\mu_1/dm_2$ in (111) has the same value as in the limiting case when $m_2 = 0$. In such cases m_1/v may be regarded as constant and we may write

$$\mu_2 = A' \log \frac{Cm_2}{v},$$

or

$$\mu_2 = C' + A' \log m_2/v, \qquad (117)$$

where

$$Cm_1/v = B, \text{ and } C' = A' \log C.$$

Suppose that the independently variable components of a homogeneous body are $S_a, \ldots S_g$ and S_h, and that the quantity of S_h is very small compared with the quantities of $S_a, \ldots S_g$ and is incapable of negative values. Then, by an extension of the argument, it can be shown that

$$\mu_h = A_h' \log \frac{C_h\, m_h}{v}, \qquad (118)$$

but A_h' and C_h may be functions not only of the temperature and pressure but also of the composition of the "solvent" (composed of $S_a, \ldots S_g$) in which S_h is dissolved. If another component S_i is also present in very small amount, it is reasonable to assume that the value of μ_h and therefore those of A_h' and C_h are nearly the same as if it were absent. Thus the potentials of components $S_h, \ldots S_k$, the quantities of which are very small compared with the quantities of $S_a, \ldots S_g$, can be expressed by equations of the form

$$\left.\begin{aligned} \mu_h &= A_h' \log \frac{C_h\, m_h}{v}, \\ \mu_k &= A_k' \log \frac{C_k\, m_k}{v}, \end{aligned}\right\} \qquad (119)\ [217]\ [218]$$

where A_h', $C_h \ldots A_k'$, C_k are functions of the temperature, the pressure and the ratios of the quantities $m_a, \ldots m_g$.

17. Derivation of the Potentials of a Solution from Their Values in a Coexistent Vapor Phase.[*] The part of the memoir which deals with the values of the potentials in gases does not come within the scope of this article, but since it is necessary for us to show how the potentials of the volatile components of a solution can be determined from the partial vapor pressures in a coexistent vapor phase we must first give a short derivation of the equation representing the variation of the potential of a gas with its pressure.

According to the laws of Charles and Boyle the pressure, volume and temperature of unit weight of a perfect gas are related according to the equation

$$pv = at,$$

where a is a specific constant for each gas. For a weight m of the gas, we have

$$pv = amt,$$

and since, according to Avogadro's law, equal numbers of molecules of all perfect gases occupy the same volume at the same temperature and pressure, this equation becomes

$$pv = \frac{Amt}{M}, \qquad (122)$$

where A is a universal constant and M the molecular weight of the gas.

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[*] Gibbs, I, 164–165.

Let ζ'', ζ' be the values of ζ for two states of the gas at the same temperature t. By (26) we have

$$\begin{aligned}\zeta'' - \zeta' &= \epsilon'' - \epsilon' - t(\eta'' - \eta') + p''v'' - p'v' \\ &= - t\,(\eta'' - \eta'),\end{aligned} \tag{123}$$

since the energy of a perfect gas at constant temperature is independent of its volume, and the product pv is also constant. In order to find the entropy change of the gas when its volume changes from v' to v'' at constant temperature, we have by (3)

$$t d\eta = p dv$$

and, introducing the value of p/t given by (122),

$$d\eta = \frac{Am}{M} \frac{dv}{v}. \tag{124}$$

Integrating this from v' to v'', we thus have

$$\eta'' - \eta' = \frac{Am}{M} \log \frac{v''}{m} - \frac{Am}{M} \log \frac{v'}{m} \tag{125}$$

or, inserting these values in (123),

$$\zeta'' + \frac{Amt}{M} \log \frac{v''}{m} = \zeta' + \frac{Amt}{M} \log \frac{v'}{m} = mC,$$

where C is a constant, which is a function of the temperature. The value of ζ for any volume v is thus given by the expression

$$\zeta = mC + \frac{Amt}{M} \log \frac{m}{v}, \tag{126}$$

and the potential of the gas is therefore

$$\mu = C + \frac{At}{M} \log \frac{m}{v} \tag{127}$$

or, by (122),

$$\mu = f(t) + \frac{At}{M} \log p. \tag{128}$$

A perfect gas mixture is one in which there is no interaction between the components, so that the energy is the sum of the energies which each component would possess if present in the same volume (and at the same temperature) by itself, and the entropy and pressure the sum of the entropies and pressures of the components separately under the same conditions.* In such a perfect gas mixture it is evident that the potential of each component is not affected by the presence of the other components and may also be represented by (127).

When a liquid and a gaseous mass are coexistent, the potentials of those components which are common to the two phases must have the same values in each. Thus, if S_2 is an actual component of coexistent liquid and vapor phases and its concentration in the vapor is $m_2^{(G)}/v^{(G)}$, its potential in the gas phase, provided that the latter has the properties of a perfect gas mixture, is given by the equation

$$\mu_2 = C_2 + \frac{At}{M_2^{(G)}} \log \frac{m_2^{(G)}}{v^{(G)}}, \tag{129}$$

and this is also the value of its potential in the liquid.

As an example of the determination of the potentials in a liquid by means of a coexistent vapor phase, we may consider a solution with two volatile components S_1 and S_2. If the partial pressures of the components in the vapor are p_1 and p_2, their potentials in the vapor by (128) are

$$\mu_1 = f_1(t) + \frac{At}{M_1^{(G)}} \log p_1, \tag{130}$$

$$\mu_2 = f_2(t) + \frac{At}{M_2^{(G)}} \log p_2, \tag{131}$$

where $M_1^{(G)}$, $M_2^{(G)}$ are the molecular weights in the vapor. These equations also give the values of the potentials in the coexistent liquid phase. At constant temperature and total applied pressure, applying (56) to the liquid phase, we have

$$m_1\, d\mu_1 + m_2\, d\mu_2 = 0,$$

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* A proof of this proposition is given by Gibbs (I, 155).

or

$$m_1 \cdot \frac{At}{M_1^{(G)}} d \log p_1 + m_2 \cdot \frac{At}{M_2^{(G)}} d \log p_2 = 0;$$

i.e.,

$$\frac{d \log p_1}{d \log p_2} = - \frac{(m_2/M_2^{(G)})}{(m_1/M_1^{(G)})}. \tag{132}$$

This equation was obtained by Duhem,* and may be used to determine the partial pressures of one component of a binary solution when the partial pressures of the other component are known.

In many cases, when the concentration of a component in the liquid phase is very small, the ratio of its concentrations in the liquid and gaseous phases is constant at a constant temperature (Henry's law), i.e.,

$$m_2^{(L)}/v^{(L)} = D\,(m_2^{(G)}/v^{(G)}), \tag{133}$$

where D is a function of the temperature. In such cases, substituting this value of $m_2^{(G)}/v^{(G)}$ in (129), we have

$$\begin{aligned} \mu_2 &= C_2 + \frac{At}{M_2^{(G)}} \log \frac{m_2^{(L)}}{Dv^{(L)}} \\ &= C_2' + \frac{At}{M_2^{(G)}} \log \frac{m_2^{(L)}}{v^{(L)}}. \end{aligned} \tag{134}$$

Henry's law is not, however, a general law of nature. From a consideration of cases in which it fails it has been shown to be probable that it holds when the molecular weight of the solute is the same in the vapour and in the solution. We may therefore substitute $M_2^{(L)}$ for $M_2^{(G)}$ in (134). There is no reason to suppose that the equation so obtained, viz.,

$$\mu_2 = C_2' + \frac{At}{M_2^{(L)}} \log \frac{m_2^{(L)}}{v^{(L)}} \tag{135}$$

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* *Compt. rend.*, **102**, 1449, (1886).

does not hold *in every case* in which the amount of the component is very small, provided that the proper value of the molecular weight in the solution is employed. The difficulty arises here that there is no independent method by which the molecular weights in solution can be determined. The general validity of (135) is based on the fact that it has been found to hold in a very large number of cases in which $M_2^{(L)}$ is given the value to be expected for simple molecules according to the chemical formula. The cumulative effect of this evidence is so strong that in doubtful cases the value of the molecular weight in solution may be determined from (135) itself.

In deducing the limiting law of the variation of the potential of a solute with its concentration we have considered a solute having an appreciable vapor pressure. But there is no reason to suppose that the behavior of involatile solutes is different in this respect and we may regard (135) as generally applicable to all components, the quantities of which cannot be negative and which are present in very small amounts, provided that the proper values of the molecular weights are used.

18. Equilibria Involving Dilute Solutions. In the last chapter of the first volume of the *Collected Works* (Gibbs I, Chap. IX) is printed a fragmentary manuscript of a proposed supplement to *The Equilibrium of Heterogeneous Substances,* in which Gibbs shows that the laws of dilute solutions obtained by van't Hoff from his law of osmotic pressure can be derived by making use of equation (135) for the potential of a solute. It will be of interest to give these demonstrations as examples of the application of the method of Gibbs to specific cases. We will consider a dilute solution formed by dissolving a small quantity, m_2 grams, of a solute S_2, in m_1 grams of a solvent S_1. The molecular weight of the solute in the solution is $M_2^{(L)}$. We will assume that the potential of S_2 in the solution is given by (135), so that under these conditions, at constant temperature and pressure

$$d\mu_2 = \frac{At}{M_2^{(L)}} \cdot \frac{v}{m_2} \cdot d\left(\frac{m_2}{v}\right). \tag{136}$$

(*a*) *Osmotic Pressure.* Suppose that this solution is separated from a quantity of the pure solvent at the same temperature by a membrane which is permeable to the solvent, but not to the solute. The difference of pressure on the two sides of the membrane is the osmotic pressure of the solution. Let the potentials of S_1 and S_2 in the solution at the temperature t and the pressure p' be μ_1' and μ_2', and the potential of S_1 in the solvent at the same temperature and pressure p'' be μ_1''. For equilibrium it is necessary that $\mu_1' = \mu_1''$. All variations in the state of the solution must satisfy (56), so that for constant temperature

$$dp' = \frac{m_1'}{v'}\, d\mu_1' + \frac{m_2'}{v'}\, d\mu_2'. \tag{137}$$

So long as the solution remains in osmotic equilibrium with the solvent in its original state, $d\mu_1' = 0$, so that

$$dp' = \frac{m_2'}{v'} \cdot d\mu_2'. \tag{138}$$

By (136)*

$$\frac{m_2'}{v'} \cdot d\mu_2' = \frac{At}{M_2^{(L)}} \cdot d\left(\frac{m_2'}{v'}\right),$$

hence, integrating (138), we obtain

$$p' - p'' = \frac{At}{v'} \cdot \frac{m_2'}{M_2^{(L)}}. \tag{139}$$

Since $\frac{At}{v'} \cdot \frac{m_2'}{M_2^{(L)}}$ is the pressure, as calculated by (122), of $m_2'/M_2^{(L)}$ gram molecules of a perfect gas in the volume v' and at temperature t, this equation expresses van't Hoff's law of osmotic pressure.†

(*b*) *Lowering of the Freezing Point.* Consider the equilibrium of the solution with a mass of the solid solvent. Applying (56) to the two phases, we have, for a variation of the solution, at constant pressure,

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* Strictly, $\frac{m_2'}{v'} \cdot d\mu_2' = \frac{m_2'}{v'} \cdot \frac{\partial \mu_2'}{\partial (m_2'/v')} \cdot d\,\frac{m_2'}{v'} + \frac{m_2'}{v'} \cdot \frac{\partial \mu_2'}{\partial p} \cdot dp$, but the last term vanishes at infinite dilution.

† *Z. physikal. Chem.*, **1**, 481 (1887). M. Planck also gave a derivation of this law, *Z. physikal. Chem.*, **6**, 187 (1890).

$$0 = \eta' dt + m_1' d\mu_1' + m_2' d\mu_2', \tag{140}$$

and for a variation of the solid phase, at constant pressure,

$$0 = \eta'' dt + m_1'' d\mu_1''. \tag{141}$$

In order to preserve equilibrium

$$d\mu_1' = d\mu_1'',$$

so that if $m_1' = m_1''$, i.e., if we take quantities of the solid and of the solution which contain equal amounts of S_1,

$$(\eta'' - \eta') dt = m_2' d\mu_2'. \tag{142}$$

Now, by (136),

$$m_2' d\mu_2' = \frac{Atv'}{M_2^{(L)}} \cdot d\left(\frac{m_2'}{v'}\right) = \frac{At}{M_2^{(L)}} \cdot dm_2',^*$$

so that, integrating (142), we obtain

$$(\eta'' - \eta')\,\Delta t = \frac{At}{M_2^{(L)}} \cdot m_2', \tag{143}$$

where Δt is the change of temperature when the value of m_2' increases from zero to its value in the given solution. Thus the lowering of the freezing point is

$$-\Delta t = \frac{At}{\eta' - \eta''} \cdot \frac{m_2'}{M_2^{(L)}} = \frac{At^2}{Q} \cdot \frac{m_2'}{m_1'\, M_2^{(L)}}, \tag{144}$$

where

$$Q = \frac{(\eta' - \eta'')\,t}{m_1'}$$

is the heat absorbed in the melting of unit weight of the solvent into the solution.†

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* The term $m_2' \dfrac{\partial \mu_2}{\partial t} \cdot dt$, which vanishes when $m_2' = 0$, is neglected here.

† van't Hoff, *Z. physikal. Chem.*, **1**, 481, (1887).

(*c*) *Lowering of the Vapor Pressure of the Solvent by an Involatile Solute.* Consider a mass of the solution in equilibrium with the vapor, in which the quantity of the solute is inappreciable. At constant temperature we have, for a variation of the solution,

$$dp = 0 + \frac{m_1'}{v'} \cdot d\mu_1' + \frac{m_2'}{v'} \cdot d\mu_2', \tag{145}$$

and for a variation of the vapor

$$dp = 0 + \frac{m_1''}{v''} \cdot d\mu_1''. \tag{146}$$

In order to preserve equilibrium, $d\mu_1' = d\mu_1''$, so that, substituting the value of $d\mu_1$ given by (146) in (145) and putting

$$\frac{m_2'}{v'} \cdot d\mu_2' = \frac{At}{M_2^{(L)}} \cdot d\left(\frac{m_2'}{v'}\right),$$

and writing

$$\frac{m_1'}{v'} = \gamma_1', \qquad \frac{m_1''}{v''} = \gamma_1'', \qquad \text{etc.,}$$

we obtain

$$dp = \frac{\gamma_1'}{\gamma_1''}\, dp + \frac{At}{M_2^{(L)}}\, d\gamma_2',$$

or

$$-\, dp = \frac{\gamma_1''}{\gamma_1' - \gamma_1''} \cdot \frac{At}{M_2^{(L)}} \cdot d\gamma_2'. \tag{147}$$

Thus, by integration,

$$p_0 - p = \frac{\gamma_1''}{\gamma_1' - \gamma_1''} \cdot \frac{At}{M_2^{(L)}} \cdot \gamma_2', \tag{148}$$

where p_0 is the value of p when $\gamma_2' = 0$. Since γ_1'' is small in comparison with γ_1', we may write, approximately,

$$p_0 - p = \frac{\gamma_1''}{\gamma_1'} \cdot \frac{At}{M_2^{(L)}} \cdot \gamma_2',$$

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and since

$$p = \frac{A\gamma_1''t}{M_1^{(G)}},$$

we have

$$\frac{p_0 - p}{p} = \frac{M_1^{(G)}}{\gamma_1'} \cdot \frac{\gamma_2'}{M_2^{(L)}} = \frac{M_1^{(G)}}{m_1'} \cdot \frac{m_2'}{M_2^{(L)}}, \tag{149}$$

i.e., the fractional lowering of the vapor pressure is equal to the ratio of the numbers of molecules of the solute and solvent. Rearranging (149), we easily obtain

$$p/p_0 = \frac{m_1'/M_1^{(G)}}{m_1'/M_1^{(G)} + m_2'/M_2^{(L)}}, \tag{150}$$

i.e., the ratio of the vapor pressure of the solution to that of the pure solvent at the same temperature is equal to the molar fraction of solvent. This is Raoult's law.* It is to be particularly noticed that the molecular weight of the solvent which appears in these equations is that in the vapor, while the molecular weight of the solute is that in the solution.

VII. The Values of Potentials in Solutions Which Are Not Very Dilute

19. Partial Energies, Entropies and Volumes. We shall now give an account of some extensions of the method of Gibbs which permit the quantitative treatment of equilibria involving concentrated solutions. The development of these extensions and the working out of practical methods for the evaluation of the potentials and other significant properties of solutions is largely due to G. N. Lewis and his collaborators.† Much of the work of these investigators has been concerned with solutions of electrolytes, which are the subject of a separate article in this volume. We shall only attempt to give in a concise form the significant extensions of Gibbs' method, with examples from solutions of non-electrolytes.

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* *Compt. rend.*, **104**, 130 (1887); *Z. physikal. Chem.*, **2**, 353 (1888).

† Outlines of a New System of Thermodynamic Chemistry, *Proc. Amer. Acad.*, **43**, 259 (1907); *Z. physikal Chem.*, **61**, 129 (1907). G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, 1923.

The exact treatment of cases of equilibrium involving actual solutions is greatly facilitated by the use of some additional quantities, which we must first introduce. Consider a solution containing $m_1, \ldots m_n$ grams of the independently variable components $S_1, \ldots S_n$, and let ϵ, η and v be the values of its energy, entropy and volume.

Then, differentiating the equation

$$\zeta = \epsilon - t\eta + pv$$

with respect to m_1, we have

$$\left(\frac{d\zeta}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}} = \left(\frac{d\epsilon}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}} - t\left(\frac{d\eta}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}} + p\left(\frac{dv}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}},$$

or

$$\mu_1 = \bar{\epsilon}_1 - t\bar{\eta}_1 + p\bar{v}_1, \tag{151}$$

where

$$\bar{\epsilon}_1 = \left(\frac{d\epsilon}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}}, \tag{152}$$

$$\bar{\eta}_1 = \left(\frac{d\eta}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}}, \tag{153}$$

and

$$\bar{v}_1 = \left(\frac{dv}{dm_1}\right)_{t,\,p,\,m_2,\,\text{etc.}}, \tag{154}$$

which represent the ratios of the increments of the energy, entropy and volume of the solution to the increase of m_1, when the temperature, pressure and quantities of $S_2, \ldots S_n$ remain constant, are called the partial values of the energy, entropy and volume for a gram of the component S_1. In the same way we may determine the partial energies, entropies and volumes for a gram of the other components. Similarly, since $\chi = \epsilon + pv$, we have

$$\bar{\chi}_1 = \bar{\epsilon}_1 + p\bar{v}_1. \tag{155}$$

At a given temperature and pressure, the quantities ϵ, η, v, χ are all homogeneous functions of the first degree with respect to $m_1, \ldots m_n$. Therefore, by (52),

$$\epsilon = m_1\bar{\epsilon}_1 + m_2\bar{\epsilon}_2 \ldots + m_n\bar{\epsilon}_n, \tag{156}$$

and, by (54),

$$m_1 d\bar{\epsilon}_1 + m_2 d\bar{\epsilon}_2 \ldots + m_n d\bar{\epsilon}_n = 0, \tag{157}$$

and similar equations may be obtained for η, v and χ.*

The variations of the potentials with pressure and temperature are easily found in terms of these quantities. Thus, by (39),

$$\left(\frac{d\zeta}{dp}\right)_{t,\, m} = v,$$

so that, differentiating this equation with respect to m_1, we have

$$\frac{\partial}{\partial m_1}\left(\frac{\partial \zeta}{\partial p}\right) = \frac{\partial v}{\partial m_1} \qquad \text{or} \qquad \frac{\partial}{\partial p}\left(\frac{\partial \zeta}{\partial m_1}\right) = \frac{\partial v}{\partial m_1},$$

i.e., expressing the invariant quantities in full,

$$\left(\frac{d\mu_1}{dp}\right)_{t,\, m} = \left(\frac{dv}{dm_1}\right)_{t,\, p,\, m_2,\, \text{etc.}} = \bar{v}_1. \tag{158}$$

Similarly, by (39),

$$\left(\frac{d\zeta}{dt}\right)_{p,\, m} = -\,\eta,$$

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* The partial molar values of these quantities are obtained by multiplying the values *per gram* given here by the molecular weight. Practical methods of evaluating the partial molar quantities have been worked out by G. N. Lewis and collaborators (G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, 1923).

whence

$$\frac{\partial}{\partial m_1}\left(\frac{\partial \zeta}{\partial t}\right) = \frac{\partial}{\partial t}\left(\frac{\partial \zeta}{\partial m_1}\right) = -\frac{\partial \eta}{\partial m_1},$$

or

$$\left(\frac{d\mu_1}{dt}\right)_{p,\,m} = -\bar{\eta}_1. \tag{159}$$

Substituting the value of $\bar{\eta}_1$ given by (151) and (153) we have

$$t\left(\frac{d\mu_1}{dt}\right)_{p,\,m} = \mu_1 - \bar{\chi}_1, \tag{160}$$

or

$$\left(\frac{d(\mu_1/t)}{dt}\right)_{p,\,m} = -\frac{\bar{\chi}_1}{t^2}. \tag{161}$$

(Compare equation (61).)

20. The Activity. The potential of a solute, the relative amount of which is very small, according to (128), is

$$\mu_1 = C + \frac{At}{M_1^{(L)}} \log \frac{m_1}{v}.$$

This relation can only be regarded as expressing the limiting law of variation of the potential with the concentration at infinite dilution, and the foregoing considerations give us no guidance as to the modifications which may be necessary at greater concentrations. In order to represent the values of the potentials in actual solutions, G. N. Lewis has introduced a quantity α, called the *activity*, which may be defined by the equation

$$\mu_1 = \mu_1^0 + \frac{At}{M_1} \log \alpha_1, \tag{162}$$

where μ_1^0 is the potential in a chosen standard state, at the same temperature and pressure, in which the activity is taken as unity. The standard state may be chosen according to the circumstances of different cases.

For example, in the case of a binary solution of the components S_1 and S_2, regarding S_1 as the solvent and S_2 as the solute, we may adopt the following conventions:

(1) The activity of the solvent is unity in the pure solvent at the same temperature and pressure, i.e.

$$\alpha_1 = N_1, \text{ when } N_1 = 1, \tag{163}$$

where

$$N_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2}$$

is the molar fraction of the solvent.

When the possible range of concentrations extends to $N_2 = 1$, as is the case with two liquids which are miscible in all proportions, the same convention may be adopted for S_2.

(2) The activity of the solute is equal to its concentration when the latter is very small. The concentration may be expressed in any suitable way. If expressed as the molar fraction (N_2), we have

$$\alpha_2 \rightarrow N_2, \text{ when } N_2 \rightarrow 0. \tag{164}$$

In the case of dilute aqueous solutions the concentration is often expressed as the number of mols ($n_2 = m_2/M_2$), dissolved in a given weight, say 1000 grams, of the solvent. The activity may then be defined so that

$$\alpha_2 \rightarrow n_2, \text{ when } n_2 \rightarrow 0^* \tag{165}$$

21. Determination of Activities from the Vapor Pressure. The potential of a volatile component of a solution is given, as in (129), by the equation

$$\mu_1 = f(t) + \frac{At}{M_{1(G)}} \log p_1,$$

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* The molecular weight to be employed in determining the activity by (162) may have any appropriate value. But if the activity is determined from the partial vapor pressure according to the method of Section 21 the molecular weight of the substance in the vapor state must be used. Also when the activity is defined by convention (2) its value can only be equal to the concentration in an infinitely dilute solution if the molecular weight is that in the solution.

where p_1 is its partial vapor pressure above the solution, and M_1 its molecular weight *in the vapor,* provided that the vapor behaves as a perfect gas. If $p_1{}^0$ be the partial vapor pressure in the standard state in which its activity is taken as unity, which we will consider to be the pure liquid at the same temperature, we have

$$\mu_1{}^0 = f(t) + \frac{At}{M_1{}^{(G)}} \log p_1{}^0,$$

so that

$$\mu_1 = \mu_1{}^0 + \frac{At}{M_1{}^{(G)}} \log \frac{p_1}{p_1{}^0}, \tag{166}$$

and by (162), taking the molecular weight as that in the vapor,

$$\alpha_1 = p_1/p_1{}^0. \tag{167}$$

When the amount of the solute is very small, it has been shown that Raoult's law,

$$p_1/p_1{}^0 = N_1, \tag{168}$$

follows from the expression (126) for the variation of the potential. It has been found by experiment that in some solutions this relation holds over the whole range of concentrations. The solutions which exhibit this behavior are usually composed of closely related substances, which might be expected to be less influenced by effects due to the interaction of the components than solutions of substances of different types or with widely differing properties. Consequently such solutions have been regarded as ideal solutions.

Therefore, when the activity is defined as in (163), $\alpha_1 = N_1$ in ideal solutions. The fraction α_1/N_1 which has been termed by G. N. Lewis the *activity coefficient,* may be regarded as a measure of the deviation of a solution from the ideal behavior. In the case of dilute solutions for which we take $\alpha_2 = n_2$, when $n_2 = 0$, the activity coefficient is taken as α_2/n_2.

Table I gives the activities and activity coefficients at 35.17°

in solutions of chloroform (S_1) and acetone (S_2) calculated from the partial vapour pressures determined by Zawidski.* For both components, the activity is taken as unity in the pure liquid.

TABLE I

Activities and Activity Coefficients in Solutions of Chloroform and Acetone (35.17°C.)

N_1	p_1	$\alpha_1 = p_1/p_1^0$	α_1/N_1	N_2	p_2	$\alpha_2 = p_2/p_2^0$	α_2/N_2
0.000	0	0.000	—	1.000	344.5	1.000	1.000
.0595	9.3	.032	0.538	0.9405	322.9	0.938	0.998
.1217	20.1	.069	.567	.8783	299.7	.871	.992
.1835	31.8	.108	.590	.8165	275.8	.801	.982
.2630	50.4	.172	.654	.7370	240.6	.699	.948
.3613	72.6	.248	.687	.6387	200.3	.582	.912
.4240	89.4	.305	.719	.5760	173.7	.504	.875
.5083	115.3	.394	.775	.4917	137.6	.400	.814
.5523	130.5	.440	.796	.4477	119.5	.347	.775
.6622	169.9	.577	.871	.3378	79.1	.230	.681
.8022	224.3	.765	.954	.1978	37.9	.110	.556
.9177	266.3	.909	.991	.0823	13.4	.039	.474
1.000	293.1	1.000	1.000	.000	0.0	0.0	—

The activities of a non-volatile component of a binary solution can be determined from the activities of a volatile component by means of the Gibbs-Duhem equation:

$$m_1 d\mu_1 + m_2 d\mu_2 = 0.$$

Since

$$\mu_1 = \mu_1^0 + \frac{At}{M_1} \log \alpha_1$$

and

$$\mu_2 = \mu_2^0 + \frac{At}{M_2} \log \alpha_2,$$

we have

$$\frac{m_1}{M_1} d \log \alpha_1 + \frac{m_2}{M_2} d \log \alpha_2 = 0. \tag{169}$$

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* *Z. physikal. Chemie*, **35**, 129 (1900).

If $m_1/M_1 = n_1$ and $m_2/M_2 = n_2$, we have

$$\log \alpha_2' - \log \alpha_2 = \int_{\alpha_1}^{\alpha_1'} - \frac{n_2}{n_1} \cdot d \log \alpha_1. \qquad (170)$$

If N_1 and N_2 are the molar fractions of the two components

$$n_1 \, d \log N_1 + n_2 \, d \log N_2 = 0 \qquad (171)$$

and, subtracting this from (169), (170) is obtained in the form

$$\log (\alpha_2'/N_2') - \log (\alpha_2/N_2) = \int_{\alpha_1/N_1}^{\alpha_1'/N_1'} - \frac{n_2}{n_1} \cdot d \log (\alpha_1/N_1). \qquad (172)$$

For example, Downes and Perman have determined the vapor pressures of water over aqueous cane sugar solutions.* From these measurements Perman† has calculated the activity coefficients of water (S_1) by (167) and those of cane sugar (S_2) by (172), taking $\alpha_2/N_2 = 1$, when $N_2 = 0$. Table II gives the values at 50°.

TABLE II

ACTIVITIES AND ACTIVITY COEFFICIENTS IN CANE SUGAR SOLUTIONS AT 50°C.

N_2	p_1 (mm. mercury)	α_1/N_1	α_2/N_2
0	92.35	1.000	1.000
0.0060	91.74	0.9999	1.000
0.0174	90.51	0.9974	1.134
0.0238	89.55	0.9933	1.269
0.0335	88.81	0.9950	1.437
0.0441	87.52	0.9914	1.624
0.0561	85.88	0.9852	1.847
0.0677	83.51	0.9699	2.053
0.1089	76.92	0.9347	2.801

22. The Lowering of the Freezing Point. Consider the equilibrium of a solution of a solute S_2 in a solvent S_1 with a solid phase consisting solely of S_1. We will denote the potentials of S_1 in the solid, the pure solvent and in the solution at a temperature t by μ_t^s, μ_t^0 and μ_t. Let t_0 be the freezing point of the pure solvent and t, the freezing point of the solution. For the equilibrium of the solid with the pure solvent at t_0 it is necessary that

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* *Trans. Faraday Soc.*, **23**, 95 (1927).

† *Ibid.*, **24**, 330 (1928).

$$\frac{\mu_{t_0}^s}{t_0} = \frac{\mu_{t_0}^0}{t_0}, \tag{173}$$

and similarly for the equilibrium of the solution with the solid at t,

$$\frac{\mu_t^s}{t} = \frac{\mu_t}{t}. \tag{174}$$

By (161)

$$\frac{d(\mu_t^s/t)}{dt} = -\frac{\chi_t^s}{t^2},$$

so that

$$\frac{\mu_t^s}{t} = \frac{\mu_{t_0}^s}{t_0} - \int_{t_0}^{t} \frac{\chi_t^s}{t^2}\cdot dt. \tag{175}$$

Similarly, for the pure solvent, we have

$$\frac{\mu_t^0}{t} = \frac{\mu_{t_0}^0}{t_0} - \int_{t_0}^{t} \frac{\chi_t^0}{t^2}\cdot dt, \tag{176}$$

and by (166), if p_1^0 and p_1 are the partial vapor pressures of S_1 over the liquid solvent and over the solution at t, and $M_1^{(G)}$ is its molecular weight in the vapor, we have

$$\frac{\mu_t}{t} = \frac{\mu_t^0}{t} + \frac{A}{M_1^{(G)}} \log (p_1/p_1^0)_t,$$

so that

$$\frac{\mu_t}{t} = \frac{\mu_{t_0}^0}{t_0} - \int_{t_0}^{t} \frac{\chi_t^0}{t^2}\cdot dt + \frac{A}{M_1^{(G)}} \log (p_1/p_1^0)_t. \tag{177}$$

Comparing (177) and (175), it is evident that

$$\frac{A}{M_1^{(G)}} \log (p_1/p_1^0)_t = \int_{t_0}^{t} \frac{\chi_t^0 - \chi_t^s}{t^2}\cdot dt. \tag{178}$$

Now, if we write $t = t_0 - \Delta t$, where Δt is the lowering of the freezing point, and represent χ_t^0 and χ_t^s as functions of the temperature by means of the equations

$$\left.\begin{aligned} \chi_t^0 &= \chi_{t_0}^0 - C_0 \cdot \Delta t, \\ \chi_t^s &= \chi_{t_0}^s - C_s \cdot \Delta t, \end{aligned}\right\} \qquad (179)$$

where C_0 and C_s are the specific heats of the pure solvent and of the solid at constant pressure, we have

$$\log\left(\frac{p_1}{p_1{}^0}\right)_t = \int_0^{\Delta t} \frac{-M_1{}^{(G)}\{(\chi_{t_0}^0 - \chi_{t_0}^s) - (C_0 - C_s)\,\Delta t\}}{A\,(t_0 - \Delta t)^2} \cdot d\Delta t. \qquad (180)$$

Here $M_1{}^{(G)}(\chi_{t_0}^0 - \chi_{t_0}^s)$ is the heat absorbed in the melting of the molecular weight of the solid solvent at t_0. For ice and water in the vicinity of 0°C., G. N. Lewis and M. Randall* have used the values

$$M_1{}^{(G)}\,(\chi_{t_0}^0 - \chi_{t_0}^s) = 1438 \text{ calories},$$

$$M_1{}^{(G)}\,(C_0 - C_s) = 9 \text{ calories},$$

and integrating the right hand member of (180) in series have obtained the expression

$$\log\,(p_1/p_1{}^0) = -\,0.009696\,\Delta t - 0.0000051\,\Delta t^2, \qquad (181)$$

which they consider accurate up to 20 or 30 degrees from the freezing point. This equation gives log $(p_1/p_1{}^0)$ or log a_1 *at the freezing point of the solution.*

Table III gives a comparison of the values of $\log(p_1/p_1{}^0)_t$ for aqueous mannite solutions, as calculated by (181) from the freezing point depressions, with the values determined directly from the vapor pressures by Frazer, Lovelace and Rogers† at 20°C.

The small differences between the two sets of values are to be ascribed to the difference between the temperatures to which they refer. The change of $\log(p_1/p_1^0)$, or $\log\alpha_1$, with temperature can be obtained by dividing equation (166) by t and differentiating. Thus we find that

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* *Thermodynamics*, p. 283 (1923).

† *J. Amer. Chem. Soc.*, **42**, 1793, (1920).

$$\frac{d\log(p_1/p_1^0)}{dt} = \frac{M_1^{(a)}}{A}\left\{\frac{d(\mu_1/t)}{dt} - \frac{d(\mu_1^0/t)}{dt}\right\}$$

$$= \frac{M_1^{(a)}}{A}\left(\frac{\bar{\chi}_1 - \chi_1^0}{t^2}\right), \tag{182}$$

where $M_1(\bar{\chi}_1 - \chi_1^0)$ is the heat absorbed when the molecular weight of the pure solvent is added to a large quantity of the solution at the temperature t. If $\bar{\chi}_1$ is known as a function of the temperature, this equation may be integrated over a considerable range of temperature, and the values of $\log(p_1/p_1^0)$ or $\log\alpha_1$ at a given temperature can be evaluated from measurements at another temperature. In the data for mannite solutions it appears that $\log(p_1/p_1^0)$ diminishes slightly as the temperature rises. In these solutions $\bar{\chi}_1 - \chi_1^0$ is therefore a small positive quantity.

TABLE III

Freezing Point Depressions and Vapor Pressure Lowerings of Aqueous Mannite Solutions

n_2	Δt	$\log(p_1/p_1^0)$ at $-\Delta t°$ (calc.)	$\log(p_1/p_1^0)$ at 20° (obs.)
0.1013	0.1874	0.00182	0.00180
0.2061	0.3807	0.00369	0.00366
0.2709	0.505	0.00489	0.00481
0.5323	0.9835	0.00953	0.00945
0.546	1.019	0.00988	0.00974

23. Osmotic Pressure of Solutions. We will consider the osmotic equilibrium of a solution of a solute S_2 in a solvent S_1 separated from the pure solvent by a membrane which is permeable to S_1 only. Let the values of the potential of S_1 at a temperature t and pressure P_0 be μ_1^0 in the solvent and μ_1 in the solution. For osmotic equilibrium, by (90), it is necessary that the potential of S_1 shall be the same on both sides of the membrane, i.e., if the pressure on the solvent remains constant, the pressure on the solution must be such that the potential of S_1 in the solution is $\mu_1{}^0$. The variation of μ_1 with pressure, according to (158), is

$$\left(\frac{d\mu_1}{dP}\right)_{t,\,m} = \bar{v}_1.$$

Therefore, if P is the pressure on the solution for osmotic equilibrium,

$$\mu_1 - \mu_1{}^0 = -\int_{P_0}^{P} \bar{v}_1 \cdot dP. \tag{183}$$

By (166), we may write

$$\mu_1 - \mu_1{}^0 = \frac{At}{M_1{}^{(G)}} \log (p_1/p_1{}^0),$$

where $p_1{}^0$ and p_1 are the partial vapor pressures of S_1 over the solvent and the solution at a total hydrostatic pressure P_0, and $M_1{}^{(G)}$ is the molecular weight of S_1 in the vapor. If we regard $\bar{v}_1$ as constant, we have

$$P - P_0 = -\frac{At}{M_1{}^{(G)}\bar{v}_1} \log (p_1/p_1{}^0),^* \tag{184}$$

where $P - P_0$ is the osmotic pressure.

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* Differentiating equation (183), we obtain

$$d\mu_1 = -\bar{v}_1 \cdot dP,$$

and since $m_1 d\mu_1 + m_2 d\mu_2 = 0$, this becomes $\frac{m_2}{m_1\bar{v}_1} . d\mu_2 = dP$, which is similar to (138), $m_1\bar{v}_1$ (the partial volume of S_1 in the solution) being substituted for the total volume of the solution. Assuming that $\bar{v}_1$ is constant, this becomes for dilute solutions which obey (136), $P - P_0 = \frac{At}{m_1\bar{v}_1} \cdot \frac{m_2}{M_2{}^{(L)}}$, which may be regarded as a more exact form of (139). This equation was obtained by G. N. Lewis, *J. Amer. Chem. Soc.*, **30**, 668 (1908). Equation (184) was derived by Berkeley, Hartley and Frazer, and by Perman and Urry from A. W. Porter's theory, *Proc. Roy. Soc.*, A, **79**, 519 (1907).

A comparison of the observed osmotic pressure of solutions of cane sugar, α-methyl glucoside and calcium ferrocyanide with values calculated from the vapor pressures by means of this equation has been made by Berkeley, Hartley and Burton,* taking for $\bar{v}_1$ the mean value between P_0 and P. The following table gives their data for solutions of cane sugar and α-methyl glucoside at 0°C.

TABLE IV

Concentration, grams sugar in 100 grams water	$\log_e(p_0/p)$	$\bar{v}_1$	Calculated osmotic pressure	Observed osmotic pressure
		Cane sugar		
56.50	0.03516	0.99515	43.91	43.84
81.20	0.05380	0.99157	67.43	67.68
112.00	0.07983	0.98690	100.53	100.43
141.00	0.10669	0.98321	134.86	134.71
		α-methyl glucoside		
35.00	0.03878	0.99810	48.29	48.11
45.00	0.05153	0.99709	64.22	63.96
55.00	0.06451	0.99579	80.50	81.00
75.00	0.09253	0.99354	115.74	115.92

Perman and Urry† have expressed $\bar{v}_1$ as a linear function of $P - P_0$, by the equation

$$\bar{v}_1 = \bar{v}_1^0\,(1 - s(P - P_0)),$$

and (184) then becomes

$$\frac{At}{M_1^{(G)}} \log\,(p_1/p_1^0) = -\int_{P_0}^{P} \bar{v}_1^0 \left\{1 - s(P - P_0)\right\} dP$$

$$= -\,\bar{v}_1^0\,(P - P_0)\left(1 - \frac{s(P - P_0)^2}{2}\right), \tag{185}$$

where the relatively small term sP_0^2 is neglected.

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* *Phil. Trans.*, **213**, 295 (1919). Osmotic pressures from *Proc. Roy. Soc.*, A, **92**, 477 (1916).

† *Proc. Roy. Soc.*, A, **126**, 44, (1930).

Table V gives a comparison of the osmotic pressures of a solution of cane sugar containing 1 gram molecule in 1000 grams solution, as calculated by equation (185), using the vapor pressure data of Perman and Downes,* with the direct determinations of Morse.†

TABLE V

CALCULATED AND OBSERVED OSMOTIC PRESSURES OF SUCROSE SOLUTIONS

Temperature	log (p_0/p)	$\bar{v}_1{}^0$	Osmotic pressure (calculated)	Osmotic pressure (observed)
30.00	—	1.002877	27.025	27.22
40.00	0.01940	1.006456	27.506	27.70
50.00	0.01914	1.010650	27.88	28.21
60.00	0.01839	1.016843	27.45	28.37
70.00	0.01848	1.0195	28.34	28.62
80.00	0.01809	1.0257	28.41	28.82

VIII. Conditions Relating to the Possible Formation of Masses Unlike Any Previously Existing‡

24. Conditions under Which New Bodies May Be Formed. So far, the only variations which have been considered possible in applying the criteria of equilibrium are those involving infinitesimal variations of the composition or state of the masses originally present. The conditions of equilibrium so obtained are obviously necessary for equilibrium but they are not always sufficient, for an infinitesimal variation of the system may also result in the formation of bodies entirely different from those originally present, and in order to discover whether the original state is one of equilibrium it is necessary to ascertain if the criteria of equilibrium are also satisfied for variations of this kind.

Gibbs defines a *new part* as one which cannot be regarded as having been formed by an infinitesimal variation in the state or composition of a part of the original mass. The new parts formed in an infinitesimal variation of the original mass are necessarily infinitely small. Let $D\epsilon$, $D\eta$, Dv, $Dm_1, \ldots Dm_n$ denote the energy, entropy, volume and the quantities of the components $S_1, \ldots S_n$ contained in any one of these new parts. We have no right to assume that a very small new part is homogeneous or that it has a definite physical boundary. Under these circumstances in order that these quantities may have a definite meaning it is necessary to define unambiguously the boundaries of the new parts. Gibbs uses a convention similar to that which he employs in the theory of capillarity. A dividing surface is drawn round each new part in such a way that it includes all the matter which is affected by the vicinity of the new part, so that the original part or parts remain strictly homogeneous right up to this boundary surface. $D\epsilon$, $D\eta$, Dv, etc., then refer to the whole of the energy, entropy, volume, etc., within the boundary surface.

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* *Trans. Faraday Soc.*, **23**, 95 (1927). The value used in the calculation at 30° is obtained from the work of Berkeley, Hartley and Burton (loc. cit.).

† *Osmotic Pressure of Aqueous Solutions*, Carnegie Institution, Washington. Publ. No. 198 (1914).

‡ Gibbs, I, 70–79.

If we use, as before, the character δ to express infinitesimal variations of the original parts of the system, the general condition of equilibrium may be written in the form

$$(\Sigma\delta\epsilon + \Sigma D\epsilon)_\eta \geqq 0 \qquad (186)\ [36]$$

or, substituting the value of $\Sigma\delta\epsilon$ taken from equation (62),

$$\Sigma D\epsilon + \Sigma t\delta\eta - \Sigma p\delta v + \Sigma\mu_1\delta m_1 \ \ldots \ + \Sigma\mu_n\delta m_n \geqq 0. \qquad (187)\ [37]$$

Making use of this equation Gibbs deduces *de novo* and by a very general argument the conditions of equilibrium when the component substances are related by r equations of the type:

$$a_1\,\mathfrak{S}_1 + a_2\,\mathfrak{S}_2 \ \ldots \ + a_n\,\mathfrak{S}_n = 0. \qquad (188)\ [38]$$

We shall consider here the simpler case in which the components S_1, $S_2, \ldots S_n$ are all independent of each other. There is no real loss of generality in this limitation for, as Gibbs points out, we may consider all the bodies originally present in the system and the new bodies which may be formed to be composed of the same *ultimate* components.

The conditions of equilibrium between the original parts of the system have already been established. They are:

$$t = T,\ p = P, \tag{189}$$

$$\mu_1 \geqq M_1, \quad \mu_2 \geqq M_2, \ \ldots \ \mu_n \geqq M_n, \tag{190}$$

i.e., the temperature and pressure have uniform values T and P throughout the system, and the potential of the component S_1 has the value M_1 in all parts of the system of which S_1 is an actual component and may have a value greater than M_1 in those parts of which it is a possible, but not an actual component. In using (187) we suppose that the total entropy and the total volume are constant, and since also in the case under consideration no component can be formed out of others the total amount of each component is also constant. The equations of condition are thus

$$\Sigma\delta\eta + \Sigma D\eta = 0, \qquad (191)\ [39]$$

$$\Sigma\delta v + \Sigma Dv = 0, \qquad (192)\ [40]$$

$$\left.\begin{array}{l} \Sigma\delta m_1 + \Sigma Dm_1 = 0, \\ \quad \cdots\cdots \\ \Sigma\delta m_n + \Sigma Dm_n = 0. \end{array}\right\} \qquad (193)$$

Inserting the values of t, p, μ_1, etc., and of $\Sigma\delta\eta$, $\Sigma\delta v$, $\Sigma\delta m_1$, etc., as given by these equations, in (187), we obtain

$$\Sigma D\epsilon - T\Sigma D\eta + P\Sigma Dv - M_1\Sigma Dm_1 \ \ldots \ - M_n\Sigma Dm_n \geqq 0, \tag{194}$$

or

$$D\epsilon - T\cdot D\eta + P\cdot Dv - M_1\cdot Dm_1 \ \ldots \ - M_n\cdot Dm_n \geqq 0, \tag{195}$$

for each of the new parts. This is the condition which must be satisfied in addition to the conditions relating to the equilibrium of the initially existing parts of the system. Gibbs shows that when there are r relations of the type (188) between the components the same condition holds, but there are then r relations of the type

$$a_1M_1 + a_2M_2 \ \ldots \ + a_nM_n = 0 \qquad (196)\ [43]$$

between the potentials.

If it could be supposed that the relation between the energy, entropy, volume and mass of the infinitely small new part were the same as that of a large homogeneous body of similar composition, the quantities $D\epsilon$, $D\eta$, Dv, Dm_1, etc., would be proportional to the energy ϵ, entropy η, volume v, masses m_1, etc., of the large body, and (195) could be written in the form

$$\epsilon - T\eta + Pv - M_1 m_1 \ \ldots \ - M_n m_n \geqq 0. \quad (197) \ [53]$$

In general however such an assumption is not permissible. For, apart from difficulties arising from the definition of the boundary surface enclosing the new part, we neglect in determining the energy, entropy, etc., of a large homogeneous body the contributions which arise from the action of capillary forces at its surfaces, and it is obviously impossible to neglect these in the case of very small bodies. Nevertheless it is probable that when (197) is satisfied, (195) is also satisfied. This appears from a consideration of the meaning of (197) in which ϵ is the energy of a body having entropy η, volume v, masses $m_1, \ldots m_n$, which is formed in a medium having the temperature T, pressure P and potentials $M_1, \ldots M_n$. Since the total entropy and volume are supposed to remain constant in the formation of this body,

$$- T\eta + Pv - M_1 m_1 \ \ldots \ - M_n m_n$$

is the change in the energy of the medium. The quantity represented in (197) is thus the energy change of the whole system in the formation of the new body, and since there is no change of entropy in the process this must be equal to the work which would be expended in the formation of the body from the medium by a reversible process. Now work must usually be expended to reduce a body to a finer state of subdivision, so that if (197) is positive or zero for a finite body there does not appear to be any reason to suppose that it will become negative even when the particles are infinitely small. So that if (197) is satisfied it appears that (195) will also be satisfied.

This argument would however break down if the energy of a mass of a body within a medium ever decreased as the size of the particles decreased (i.e., in cases of negative surface tension).

Substances which exhibit the phenomenon of *peptisation*, i.e., when a large mass of a substance spontaneously breaks up into small particles, may be examples of such behavior. However in such a case large masses of the substance in the given medium would be inherently unstable and there would be no advantage in substituting (197) for (195).

It is evident that (197) cannot be regarded as a necessary condition of equilibrium, for (195) may be satisfied and the system will therefore be in a state of equilibrium even when (197) is unsatisfied. Cases of this kind are met with in superheated liquids, supersaturated solutions, etc. In the case of a supersaturated solution of a given substance (197) is negative, but we must suppose that on account of capillary forces etc. the separation of an infinitely small quantity would give rise to positive (or zero) value in (195). It is however difficult to distinguish between effects of this kind and "passive resistances" to change. Gibbs remarks that "such an equilibrium will, however, be *practically* unstable. By this is meant that, although, strictly speaking, an infinitely small disturbance or change may not be sufficient to destroy the equilibrium, yet a very small change in the initial state, perhaps a circumstance which entirely escapes our powers of perception, will be sufficient to do so. The presence of a small portion of the substance for which the condition [53] does not hold true, is sufficient to produce this result, when this substance forms a variable component of the original homogeneous masses. In other cases, when, if the new substances are formed at all, different kinds must be formed simultaneously, the initial presence of the different kinds, and that in immediate proximity, may be necessary."

25. Generalized Statement of the Conditions of Equilibrium. The conditions of equilibrium of the parts initially present, and with respect to the formation of new parts, may be summed up as follows. Since for any homogeneous mass, by (48), the equation

$$\epsilon - t\eta + pv - \mu_1 m_1 - \mu_2 m_2 \ \ldots \ - \mu_n m_n = 0, \qquad (198)$$

holds when $m_1, m_2, \ldots m_n$ refer to the *ultimate* components of the mass, the condition of equilibrium between the original parts can be expressed by the conditions that it shall be possible to give to T, P, $M_1, \dots M_n$ in

$$\epsilon - T\eta + Pv - M_1m_1 - M_2m_2 \dots - M_nm_n \qquad (199)$$

such values that the value of this expression shall be zero for *every* homogeneous part of the system. The equilibrium is practically stable if

$$\epsilon - T\eta + Pv - M_1m_1 - M_2m_2 \dots - M_nm_n \geqq 0 \quad (200)$$

for any other body which may be formed from the same components, and this condition may be united with the former one in the statement that it shall be possible to give T, P, $M_1, \dots M_n$ such values that the value of (200) for each homogeneous part of the system shall be as small as for any body whatever made of the same components.

IX. The Internal Stability of Homogeneous Fluids*

26. General Tests of Stability. Consider a homogeneous fluid, the ultimate components $S_1, S_2, \dots S_n$ of which are present in the amounts $m_1, m_2, \dots m_n$. The conditions imposed in deducing the conditions of equilibrium are fulfilled if we suppose that the fluid is contained in a rigid envelop which is a non-conductor of heat and impervious to all its components. The conditions (199) and (200) might be employed to determine the stability of the fluid, but it is desirable to formulate them in a somewhat more general manner, since for the stability of the fluid it is necessary that it shall be in equilibrium both with respect to the formation of new parts as defined in the last section, and also with respect to the formation of phases which may only differ infinitesimally from the original phase of the body. Gibbs states the condition of stability as follows:

"*If it is possible to assign such values to the constants T, P, $M_1, M_2, \dots M_n$ that the value of the expression*

$$\epsilon - T\eta + Pv - M_1m_1 - M_2m_2 \dots - M_nm_n \quad (201)\ [133]$$

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* Gibbs, I, 100-105.

shall be zero for the given fluid, and shall be positive for every other phase of the same components, i.e., for every homogeneous body not identical in nature and state with the given fluid (but composed entirely of [some or all of the substances] S_1, $S_2, \ldots S_n$), *the condition of the given fluid will be stable.*"

The following proof may be given of this proposition. It is evident that if (201) is positive for every other phase of the components, its value for the whole mass must be positive when the latter is in any other than its given condition. The value of (201) is therefore less when the mass is in the given condition than when it is in any other condition. Since on account of the conditions imposed by the surrounding envelop neither the entropy, volume, or the quantities m_1, $m_2, \ldots m_n$ for the whole mass can change, it follows that the energy in the given condition is less than that in any other condition of the same entropy and volume. The given condition, by (5), is therefore stable.

Since (201) is zero when applied to the given fluid (i.e., when ϵ is the energy, η the entropy, v the volume, $m_1, \ldots m_n$ the quantities of the components of the given fluid), it is evident that T is its temperature, P its pressure, and M_1, $M_2, \ldots M_n$ the potentials of its components in the given state. If we wish to test the stability of the fluid with respect to the formation of some other phase we must insert for ϵ, η, v, m_1, etc. the values of the energy, entropy, volume, and masses in a mass of the phase in question (not necessarily at the same temperature and pressure). If there is no other phase of the components for which the quantity so obtained has a positive value the given fluid is stable.

It has already been shown that the expression (201) represents the reversible work which must be expended in forming a phase of energy ϵ, entropy η, volume v and masses m_1, $m_2, \ldots m_n$ within a medium having the temperature T, pressure P, potentials M_1, $M_2, \ldots M_n$. The condition of stability therefore amounts to this: the fluid is stable if no other phase can be formed in it without the expenditure of work.

When the value of the expression (201) is zero for the given fluid and negative for some other phase of the same components it is evident that the fluid is unstable. It may also happen that while T, P, M_1, $M_2, \ldots M_n$ may be given such values that (201) is zero for the given fluid there is some other phase for which (201) is also zero. This other phase must obviously have the same temperature and pressure, and the same values of the potentials, and is therefore a phase which could coexist with the given fluid. But Gibbs points out that although there may be phases which can coexist with the given mass, it is highly improbable that such phases could be formed within the given mass without a change of entropy or of volume. Thus although at the triple point water can coexist with ice and vapor, a quantity of water in this state enclosed in an envelop which has a constant volume and is impervious to heat is quite stable.

27. Condition of Stability at Constant Temperature and Pressure. In considering whether (201) is capable of a negative value for any phase, Gibbs points out that it is only necessary to consider phases which have the temperature T and the pressure P. For it may be assumed that the mass is capable of at least one state of not unstable equilibrium at this temperature and pressure, and in such a state the value of (201) must be as small as for any other state of the same matter. Therefore, if (201) is capable of a negative value, it will have a negative value at the temperature T and the pressure P. Also, if it is not capable of a negative value, any state for which it has the value zero must have the temperature T and the pressure P.

For any body at the temperature T and the pressure P, (201) reduces to

$$\zeta - M_1m_1 - M_2m_2 \ldots - M_nm_n, \qquad (202)\ [135]$$

and in this form is capable of a very direct application, which is the basis of the geometrical methods employed by Gibbs in his use of curves and surfaces.

Consider a series of homogeneous phases containing the two components S_1 and S_2 in different proportions. The ζ-curve for a constant temperature t and pressure p is obtained by plotting the values of ζ for the unit mass of the different phases (i.e., $m_1 + m_2 = 1$) against the composition. Thus the point Z (Fig. 5) represents a phase for which

$$\frac{m_2}{m_1 + m_2} = \frac{XZ}{XY},$$

and the value of ζ for this phase is represented by ZE. The curve AB represents the values of ζ for all homogeneous phases

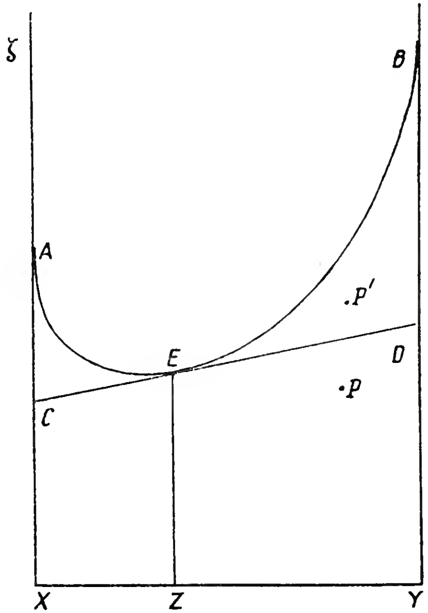

FIG. 5

when the composition is varied from that of the phase for which $m_1 = 1$ (represented by point X) to that for which $m_2 = 1$ (point Y). CD is the tangent to the ζ curve at the point E. It can be shown that intercepts made by this tangent on the axes at X and Y are equal to the values of M_1 and M_2 for the phase represented by E, i.e., $XC = M_1$ and $YD = M_2$.* The value of $m_1M_1 + m_2M_2$ for any given values of m_1 and m_2 (for which $m_1 + m_2 = 1$) is therefore represented by the point on the line CD corresponding to these values. The expression

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* If the potentials of S_1 and S_2 in the phase E are μ_1 and μ_2, the tangent CD is characterized by the equation $d\zeta = \mu_1 dm_1 + \mu_2 dm_2$, or since when

$$\zeta - M_1m_1 - M_2m_2 \tag{203}$$

is positive for every other phase of the components, other than the one under consideration, when there is no phase for which the value of ζ, at the same temperature and pressure, lies below the line CD. Thus if the two components form a solid compound, of which the composition and value of ζ are represented by the point P (under CD), the phase E will be unstable (supersaturated) with respect to this phase, for $\zeta - M_1m_1 - M_2m_2$ is negative for the phase P. But if the point representing this phase is above CD (say at P'), $\zeta - M_1m_1 - M_2m_2$ will be positive, and the phase E will be stable in respect to the formation of this phase. Similarly if the curve AB is everywhere above the tangent CD, except at the single point of contact, the phase E is stable with respect to the other homogeneous phases, and cannot split into any of the phases represented by the points of this curve.

28. Condition of Stability Referred to the Pressure of Phases for Which the Temperature and Potentials Are the Same as Those of the Phase in Question. In the expression

$$\epsilon - T\eta + Pv - M_1m_1 - M_2m_2 - \ \ldots \tag{204}$$

T, P, M_1, M_2, etc. are the temperature, pressure and potentials in the fluid mass the stability of which is in question, and ϵ, η, v, m_1, m_2, etc. are the energy, entropy, volume, etc. of a given phase with regard to which the stability is being tested. These quantities are related by the equation

$$\epsilon = t\eta - pv + \mu_1m_1 + \mu_2m_2 + \ \ldots, \tag{205}$$

where t is the temperature, p the pressure and μ_1, μ_2, etc., the potentials in the given phase. If we consider only phases for

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$m_1 + m_2 = 1$, $dm_1 = -dm_2$, the slope of the tangent is given by $d\zeta = (\mu_2 - \mu_1)dm_2$. Since $ZE = \mu_1m_1 + \mu_2m_2$, $XC = \mu_1m_1 + \mu_2m_2 - (\mu_2 - \mu_1)m_2 = \mu_1$. Similarly $YD = \mu_2$.

which $t = T$, $\mu_1 = M_1$, $\mu_2 = M_2$, etc., we may by substituting the value of ϵ given by (205), reduce (204) to the expression

$$(P - p)v. \tag{206}$$

In order to justify the use of this expression it is necessary to show that in testing the stability of a fluid it is sufficient to take into account only phases for which the temperature and potentials are the same as in the given fluid. This can be done by considering the least value of which (201) is capable at a *constant value of v*. Suppose that (201) has its smallest possible value, without any restriction, when evaluated for a phase having the energy ϵ, entropy η, volume v, masses $m_1, \ldots m_n$.* Then if ϵ', η', v', m_1', m_2', $\ldots m_n'$ are the values referring to any other phase we have

$$\begin{aligned} &\epsilon' - T\eta' + Pv' - M_1m_1' - M_2m_2' \ldots - M_nm_n' \\ &\geqq \epsilon - T\eta + Pv - M_1m_1 - M_2m_2 \ldots - M_nm_n \end{aligned}$$

or, if both phases have the same volume,

$$\epsilon' - \epsilon - T(\eta' - \eta) - M_1(m_1' - m_1) - M_2(m_2' - m_2) \ldots \geqq 0.$$

Thus if the second phase can be considered as having been formed by an infinitesimal variation of the first phase, at constant volume, we may write this equation as

$$d\epsilon - Td\eta - M_1dm_1 - M_2dm_2 \ldots \geqq 0. \tag{207}$$

But a variation of the energy of the first phase, at constant volume, is given by

$$d\epsilon = td\eta + \mu_1dm_1 + \mu_2dm_2 + \ldots, \tag{208}$$

and (207) and (208) can only both hold if

$$t = T, \quad \mu_1 = M_1, \quad \mu_2 = M_2, \quad \text{etc.}$$

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* It is supposed here that the components of the body are some or all of the components $S_1, S_2, \ldots S_n$. Gibbs considers the case in which the components of the new phase may be different from those of the given fluid.

Therefore the phase for which (201) has the least value will be found among those having the temperature T and potentials M_1, M_2, etc., and in determining the stability of the given fluid we need only consider phases in which the temperature and potentials have these values. In this case the given fluid will be stable unless the expression (206) is capable of having a negative value.

The conditions of stability are thus stated by Gibbs in the following very simple form:

"If the pressure of the fluid is greater than that of any other phase of the same components which has the same temperature and the same values of the potentials for its actual components, the fluid is stable without coexistent phases; if its pressure is not as great as some other such phase, it will be unstable; if its pressure is as great as that of any other such phase, but not greater than that of every other, the fluid will certainly not be unstable, and in all probability it will be stable (when enclosed in a rigid envelop which is impermeable to heat and to all kinds of matter), but it will be one of a set of coexistent phases of which the others are the phases which have the same pressure."

For example, consider a solution of carbon dioxide in water. If the pressure of a vapor phase at the same temperature, and in which carbon dioxide and water have the same potentials as in the solution, is greater than the pressure of the solution, the latter is unstable; but if the pressure of a vapor phase which satisfied these conditions is less than that of the solution, the latter is stable (with respect to the formation of a vapor phase). A vapor phase containing carbon dioxide and water at the same potentials as in the solution, and having the same temperature and pressure could obviously coexist with the solution, but a quantity of such a solution in a confined space is stable.

X. Stability in Respect to Continuous Changes of Phase*

29. General Remarks. In order to test whether a homogeneous fluid is stable with respect to the formation of phases which differ from it infinitely little (which are termed by Gibbs, adjacent phases), we may apply to such changes the same general test as before. It is evidently only necessary to consider as the component substances of such phases the independently variable components of the given fluid. The constants M_1, M_2, etc. in (201) have the values of the potentials for these components in the given fluid, for which the value of (201) is necessarily zero. Then, *if for any infinitely small variation of the phase the value of (201) can become negative, the fluid will be unstable; but if for every infinitely small variation of the phase (201) becomes positive, the fluid will be stable.* Gibbs points out that the case in which the phase can be varied without altering the value of (201) can hardly be expected to occur. For, in such a case, the phase concerned would have coexistent adjacent phases.

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* Gibbs, I, 105–115.

This condition, which Gibbs calls the condition of stability, may be written in the form

$$\epsilon'' - t'\eta'' + p'v'' - \mu_1'm_1'' \ \ldots \ - \mu_n'm_n'' > 0, \qquad (209)\,[142]$$

where t', p', μ_1', μ_2', etc. are the temperature, pressure and the potentials in the phase, the stability of which is in question, and ϵ'', η'', v'', m_1'', m_2'', etc., are the energy, entropy, volume and quantities of the components in any adjacent phase. Single accents are used to distinguish quantities referring to the first phase, and double accents those referring to the second.

Particular conditions of stability can be obtained by transforming this equation in various ways.

30. Condition with Respect to the Variation of the Energy. If we add

$$-\epsilon' + t'\eta' - p'v' + \mu_1'm_1' + \mu_2'm_2' \ \ldots \ + \mu_n'm_n' = 0,$$

to (209), we obtain

$$(\epsilon'' - \epsilon') - t'(\eta'' - \eta') + p'(v'' - v') - \mu_1'(m_1'' - m_1') \\ -\mu_2'(m_2'' - m_2') \ \ldots \ > 0, \qquad [143]$$

which may be written in the form

$$\Delta\epsilon > t\Delta\eta - p\Delta v + \mu_1\Delta m_1 + \mu_2\Delta m_2 \ \ldots \ + \mu_n\Delta m_n, \quad (210)\ [145]$$

where the character Δ is used to signify that the condition, although relating to infinitesimal differences, is not to be interpreted in accordance with the usual convention in differential equations, in which infinitesimals of higher orders than the first are neglected, but is to be interpreted *strictly*, like an equation between finite differences. (See page 72.) When applying the condition (210), it is necessary that the quantities $\Delta\epsilon$, $\Delta\eta$, Δm_1, etc., should be such as are determined by an actual change of phase and not by a change in the total amount of the phase, for in that case the term on the left of (210) is zero. This can be accomplished by making v constant, and then dividing the remaining terms by the constant v. Then we have

$$\Delta\frac{\epsilon}{v} > t\,\Delta\frac{\eta}{v} + \mu_1\,\Delta\frac{m_1}{v} + \mu_2\,\Delta\frac{m_2}{v} \ldots + \mu_n\,\Delta\frac{m_n}{v}. \qquad (211)\ [146]$$

But according to (44) we have

$$d\frac{\epsilon}{v} = t\,d\frac{\eta}{v} + \mu_1\,d\frac{m_1}{v} + \mu_2\,d\frac{m_2}{v} \ldots + \mu_n\,d\frac{m_n}{v}, \qquad (212)\ [147]$$

so that, "*the stability of any phase in regard to continuous changes depends upon the same conditions in regard to the second and higher differential coefficients of the density of energy regarded as a function of the density of entropy and the densities of the several components, which would make the density of energy a minimum, if the necessary conditions in regard to the first differential coefficients were fulfilled.*"

In a phase of one component, it is more convenient to make m constant instead of v, when (210) becomes

$$\Delta\epsilon > t\Delta\eta - p\Delta v.$$

The meaning of this condition can be seen if the values of ϵ, η and v are represented by rectangular coordinates. Let D

represent a phase having energy ϵ, entropy η and volume v (Fig. 6). The points representing adjacent phases form a surface. Let E be a point on this surface, representing a phase having the energy $\epsilon + \Delta\epsilon$, entropy $\eta + \Delta\eta$ and volume $v + \Delta v$.

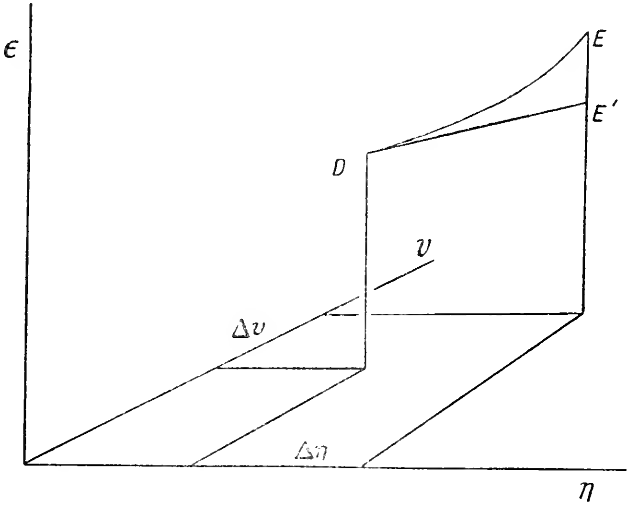

FIG. 6

If the tangent plane to the surface through the point D, cuts the vertical line through E at E', the ordinate of the point E' is

$$\epsilon + \frac{d\epsilon}{d\eta}\Delta\eta + \frac{d\epsilon}{dv}\Delta v.$$

Since

$$\frac{d\epsilon}{d\eta} = t, \ \frac{d\epsilon}{dv} = -p,$$

the vertical distance EE' is thus equal to $\Delta\epsilon - t\Delta\eta + p\Delta v$. Thus, (210) is positive when the ϵ, η, v surface for adjacent phases lies above the tangent plane, taken at the point representing the phase in question. Any phase for which this holds true is stable with respect to continuous changes.

31. Condition with Respect to the Variation of the Pressure. Substituting the value

$$\epsilon'' = t''\eta'' - p''v'' + \mu_1''m_1'' \ldots + \mu_n''m_n''$$

in (209), we obtain

$$\begin{aligned} - \eta''(t' - t'') + v''(p' - p'') - m_1''(\mu_1' - \mu_1'') \\ - m_2''(\mu_2' - \mu_2'') \ldots > 0. \end{aligned} \qquad (213)\ [144]$$

This formula expresses the condition of stability for the phase to which t', p', etc. relate. But if all phases (within any given limits) are stable, (213) will hold for any two infinitesimally differing phases (within the same limits) and the phase ($''$) may be regarded as the phase of which the stability is in question, and ($'$) as the infinitestimal variant of it. Then (213) can be written

$$- \eta\Delta t + v\Delta p - m_1\Delta\mu_1 \ \ldots \ - m_n\Delta\mu_n > 0, \quad (214)\ [148]$$

or

$$\Delta p > \frac{\eta}{v}\Delta t + \frac{m_1}{v}\Delta\mu_1 \ldots + \frac{m_n}{v}\Delta\mu_n. \quad (215)\ [149]$$

But by (56)

$$dp = \frac{\eta}{v}dt + \frac{m_1}{v}d\mu_1 \ldots + \frac{m_n}{v}d\mu_n, \qquad (216)$$

so that "we see that it is necessary and sufficient for the stability in regard to continuous changes of all the phases within any given limits, that within those limits the same conditions should be fulfilled in respect to the second and higher differential coefficients of the pressure regarded as a function of the temperature and the several potentials, which would make the pressure a minimum, if the necessary conditions with regard to the first differential coefficients were fulfilled."

32. Conditions of Stability in Terms of the Functions ψ and ζ. Writing

$$\epsilon'' = \psi'' + t''\eta'',$$

and

$$-\psi' - p'v' + \mu_1'm_1' \;\ldots\; + \mu_n'm_n' = 0,$$

(209) becomes

$$(\psi'' - \psi') + (t'' - t')\eta'' + (v'' - v')p' - (m_1'' - m_1')\mu_1' \;\ldots\; - (m_n'' - m_n')\mu_n' > 0. \qquad (217)\ [150]$$

As in (213), when all phases within any given limits are stable, this condition holds for any two phases which differ infinitely little. When

$$v' = v'',\ m_1' = m_1'',\ \ldots\ m_n' = m_n'',$$

$$(\psi'' - \psi') + (t'' - t')\eta'' > 0, \qquad (218)\ [151]$$

or

$$(\psi' - \psi'') + (t' - t'')\eta'' < 0, \qquad (219)$$

which may be written

$$[\Delta\psi + \eta\Delta t]_{v,\,m} < 0. \qquad (220)\ [153]$$

Note that the phase, the stability of which is in question here is that to which η'' refers; hence $\Delta\psi = \psi' - \psi''$. Similarly, when $t' = t''$,

$$(\psi'' - \psi') + p'(v'' - v') - \mu_1'(m_1'' - m_1') \;\ldots\; - \mu_n'(m_n'' - m_n') > 0, \qquad (221)\ [152]$$

or

$$[\Delta\psi + p\Delta v - \mu_1\Delta m_1 \;\ldots\; - \mu_n\Delta m_n]_t > 0. \qquad (222)\ [154]$$

The phase of which the stability is in question is now that distinguished by single accents.

We may first observe that since, by (45), $(d\psi/dt)_{v,\,m} = -\eta$, (220) requires that $d^2\psi/dt^2 < 0$, i.e., $d\eta/dt$ or $td\eta/dt$ is positive, $td\eta/dt$ being the specific heat of the phase in question at constant volume. Secondly, when the composition of the body remains unchanged, (222) becomes

$$[\Delta\psi + p\Delta v]_{t,\,m} > 0, \qquad (223)\ [160]$$

and since, by (45), $(d\psi/dv)_{t,\,m} = -p$, this implies that $(d^2\psi/dv^2)_{t,\,m} > 0$ or dp/dv must be negative. The conditions (220) and (223) thus express the conditions of thermal and mechanical stability of the body.

The meaning of condition (222), as applied to the ψ-v-m diagram for constant temperature, easily follows from considerations similar to those used in connection with (211).

Again, by (15) and (50), (209) becomes

$$(\zeta'' - \zeta') + \eta''(t'' - t') - v''(p'' - p')$$
$$- \mu_1'(m_1'' - m_1') \ \ldots \ - \mu_n'(m_n'' - m_n') > 0, \qquad (224)\ [161]$$

from which we may obtain the conditions

$$[\Delta\zeta + \eta\Delta t - v\Delta p]_m < 0, \qquad (225)\ [162]$$

and

$$[\Delta\zeta - \mu_1\Delta m_1 \ \ldots \ - \mu_n\Delta m_n]_{t,\,p} > 0. \qquad (226)\ [163]$$

In order to show the meaning of this condition, we will consider the ζ-composition diagram, for constant temperature and pressure, of a two component system.* It is convenient in graphical representations (as in Fig. 7), to use as the variables expressing composition the fractional weights of the components. If we limit ourselves to phases for which $m_1 + m_2 = 1$, the quantities m_1 and m_2 become equal to the fractional weights. Then for any change of phase, $\Delta m_1 = -\Delta m_2$. The curve AB (Fig. 7) represents the ζ-values of homogeneous phases, at constant temperature and pressure, when m_2 is varied from 0 to 1. Let the coordinates of the point D be ζ, m_2 and the coordinates of an adjacent point E be $\zeta + \Delta\zeta$, $m_2 + \Delta m_2$. Let ST be the tangent to the curve AB, at the point D. The slope of this tangent is given by $d\zeta/dm_2 = \mu_2 - \mu_1$, so that if E' is its point of intersection with the vertical through E, the ordinate of E' is $\zeta + (\mu_2 - \mu_1)\Delta m_2$ or $\zeta + \mu_2\Delta m_2 + \mu_1\Delta m_1$, since $\Delta m_2 = -\Delta m_1$. If $\Delta\zeta > \mu_2\Delta m_2 + \mu_1\Delta m_1$, the point E is above the point E'. Therefore the condition of stability of the phase D, with respect to continuous changes, is that the ζ-curve for adjacent phases shall be above the tangent at D, except at the single point of contact.

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* Compare also Article H of this volume.

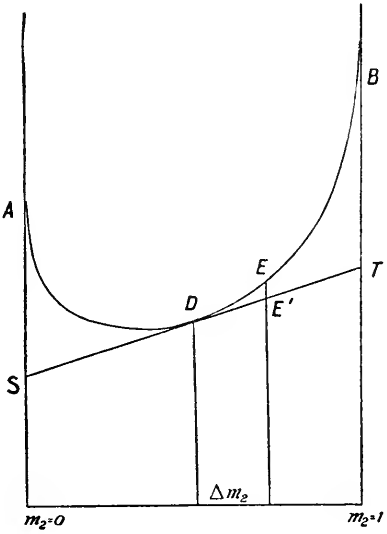

FIG. 7

33. Conditions with Respect to Temperature and the Potentials. Since (213) holds true of any two infinitesimally differing phases, within the limits of stability, we may combine this condition, viz.,

$$\eta''(t'' - t') - v''(p'' - p') + m_1''(\mu_1'' - \mu_1')$$
$$\ldots + m_n''(\mu_n'' - \mu_n') > 0,$$

and the condition obtained by interchanging the single and double accents, i.e.,

$$\eta'(t' - t'') - v'(p' - p'') + m_1'(\mu_1' - \mu_1'')$$
$$\ldots + m_n'(\mu_n' - \mu_n'') > 0,$$

in the condition

$$(t'' - t')(\eta'' - \eta') - (p'' - p')(v'' - v') + (\mu_1'' - \mu_1')(m_1'' - m_1') \\ \ldots + (\mu_n'' - \mu_n')(m_n'' - m_n') > 0, \qquad (227)\ [170]$$

which may be written in the form

$$\Delta t \Delta \eta - \Delta p \Delta v + \Delta \mu_1 \Delta m_1 \ \ldots + \Delta \mu_n \Delta m_n > 0. \qquad (228)\ [171]$$

This must hold true of any two infinitesimally differing phases within the limits of stability. If we give the value zero to one of the differences in every term except one, it is evident that the values of the two differences in the remaining term must have the same sign, except in the case of Δp and Δv, which have opposite signs. Thus we have, for example,

$$\left(\frac{\Delta t}{\Delta \eta}\right)_{v,\, m_1, \ldots m_n} > 0; \qquad (229)\ [166]$$

$$\left.\begin{array}{ll} \left(\frac{\Delta \mu_1}{\Delta m_1}\right)_{t,\, v,\, m_2, \ldots m_n} > 0, & [167] \\ \left(\frac{\Delta \mu_2}{\Delta m_2}\right)_{t,\, v,\, \mu_1,\, m_3, \ldots m_n} > 0, & [168] \\ \cdots\cdots\cdots\cdots\cdots\cdots & \\ \left(\frac{\Delta \mu_n}{\Delta m_n}\right)_{t,\, v,\, \mu_1,\, \mu_2, \cdots \mu_{n-1}} > 0; & [169] \end{array}\right\} \qquad (230)$$

and

$$\left(\frac{\Delta p}{\Delta v}\right)_{t,\, m_1, \ldots m_n} < 0. \qquad (231)$$

Thus, when v, m_1, $\ldots m_n$ have any given constant values, within the limits of stability, t is an *increasing function* of η; and when t, v, m_2, $\ldots m_n$ have any given constant values, within the limits of stability, μ_1 is an *increasing function* of m_1, etc. In general, "*within the limits of stability, either of the two quantities occurring (after the sign* Δ) *in any term of* [*171*] *is an increasing function of the other,—except* p *and* v, *of which the opposite is true,—when we regard as constant one of the quantities* *occurring in each of the other terms, but not such as to make the phases identical.*"

It is evident that when v is taken as constant, there are a number of ways in which one of the quantities in each of n of the remaining $n + 1$ terms can be made zero. We can thus obtain different sets of $n + 1$ conditions, like (229) and (230). Gibbs points out that it is not always possible to substitute the condition that the pressure shall be constant for the condition that the volume shall be constant, without imposing a restriction on the variations of the phase.

It may be pointed out with regard to the equations (229), (230), that if the sign Δ is replaced by d we obtain conditions which are *sufficient* for stability.

It is evident that if

$$\left(\frac{d\mu_n}{dm_n}\right)_{t,\, v,\, \mu_1,\, \ldots\, \mu_{n-1}} > 0, \tag{232}$$

the condition

$$\left(\frac{\Delta\mu_n}{\Delta m_n}\right)_{t,\, v,\, \mu_1,\, \ldots\, \mu_{n-1}} > 0 \tag{233}$$

must also hold true, i.e., the condition of stability is satisfied. But (233) may also hold true if

$$\left(\frac{d\mu_n}{dm_n}\right)_{t,\, v,\, \mu_1,\, \ldots\, \mu_{n-1}} = 0 \tag{234}$$

(when one or more of the higher differential coefficients are positive). The expression (233) cannot hold true when the differential coefficient term (232) is negative, so that it is *necessary* for stability that

$$\left(\frac{d\mu_n}{dm_n}\right)_{t,\, v,\, \mu_1,\, \ldots\, \mu_{n-1}} \geqq 0. \tag{235}$$

34. Limits of Stability. At the limits of stability (i.e., the limits which divide stable from unstable phases) with respect to continuous changes, one of the conditions (229), (230) must cease to hold true. Therefore, one of the differential coefficients like that in (234) must be zero.

The differential coefficients

$$\frac{dt}{d\eta}, \frac{d\mu_1}{dm_1}, \dots \frac{d\mu_n}{dm_n}, \qquad (236)\ [181]$$

may be evaluated in a number of different ways, according to whether the quantities which are to remain constant are chosen from the numerators or the denominators of the other terms. Gibbs shows that when the quantites which, together with v, are to remain constant are taken from the *numerators* of the others, their values will be at least as small as when one or more of the constants are taken from the denominators.

At least one of the coefficients determined in this way will therefore be zero. But if one of these coefficients is zero it can be shown that all the others, having their constants chosen in the same way, will also be zero. Gibbs gives the following proof of this proposition. "For if

$$(d\mu_n/dm_n)_{t,\, v,\, \mu_1,\, \dots\, \mu_{n-1}}, \qquad (237)\ [182]$$

for example, has the value zero, we may change the density of the component S_n without altering (if we disregard infinitesimals of higher orders than the first) the temperature or the potentials, and therefore, by [98], without altering the pressure. That is, we may change the phase without altering any of the quantities t, p, μ_1, $\dots \mu_n$. Now this change of phase, which changes the density of one of the components, will in general change the density of the others and the density of entropy. Therefore, all the other differential coefficients formed after the analogy of [182], i.e., formed from the fractions in [181] by taking as constants for each the quantities in the numerators of the others together with v, will in general have the value zero at the limit of stability. And the relation which characterizes the limit of stability may be expressed, in general, by setting any one of these differential coefficients equal to zero."

We may write this condition in the form

$$\left[\frac{d\mu_n}{d(m_n/v)}\right]_{t,\, \mu_1,\, \dots\, \mu_{n-1}} = 0, \qquad (238)\ [183]$$

or

$$\left[\frac{d(m_n/v)}{d\mu_n}\right]_{t,\,\mu_1,\,\ldots\,\mu_{n-1}} = \infty. \qquad (239)\ [184]$$

But, by (56),

$$m_n/v = (dp/d\mu_n)_{t,\,\mu_1,\,\ldots\,\mu_{n-1}},$$

so that (239) becomes

$$\frac{d^2p}{d\mu_n^{\,2}} = \infty. \qquad (240)\ [185]$$

Similarly, we may obtain

$$\frac{d^2p}{dt^2} = \infty, \qquad \frac{d^2p}{d\mu_1^{\,2}} = \infty, \ldots \frac{d^2p}{d\mu_{n-1}^2} = \infty. \qquad (241)\ [186]$$

"Any one of these equations [185], [186], may be regarded, in general, as the equation of the limit of stability. We may be certain that at every phase at that limit one at least of these equations will hold true."

XI. Critical Phases*

35. Number of Degrees of Freedom of a Critical Phase. A critical phase is defined as one at which the distinction between two coexistent phases vanishes. For example, at the critical point of water, the liquid phase and the vapor phase become identical. Again, in Figure 8, the curves *CA* and *CB* represent the compositions of the two coexistent liquid phases in the system phenol-water at different temperatures at a constant pressure. As the temperature rises, the curves representing the compositions of the two coexistent phases approach each other, and at the point *C* the two phases become identical. Similar phenomena are met with in ternary mixtures. Let S_1 and S_2 be two liquids which are incompletely miscible at a certain temperature and pressure, but which both form homogeneous solutions in all proportions with a third liquid S_3. If we add

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* Gibbs, I, 129–131.

S_3 to the two coexistent phases containing S_1 and S_2, we shall obtain a series of two coexistent ternary phases, terminating in a phase at which the two phases become identical.

Let n be the number of independently variable components. According to the phase rule, a pair of coexistent phases has n degrees of freedom, i.e., is capable of n independent variations. Thus, in the case of phenol and water, a pair of coexistent phases can be varied independently in two ways, i.e., we can vary both the temperature and the pressure without making one phase disappear. Now if we keep the pressure constant and vary the temperature, we shall obtain a series of coexisting phases *terminating in the critical phase.* At a slightly different pressure there is a similar series of coexisting phases, terminating in a slightly different critical phase. It is evident that the number of independent variations of which the critical phase is capable is one less than that of the two coexistent phases, i.e., the number of independent variations of a critical phase, *while remaining as such,* is $n - 1$.

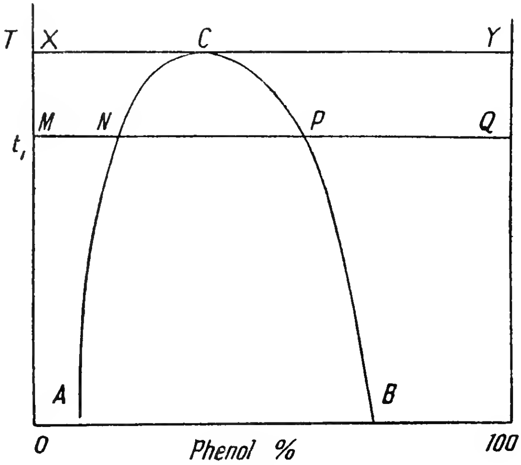

FIG. 8

36. Conditions in Regard to Stability of Critical Phases. "The quantities, t, p, μ_1, μ_2, . . . μ_n have the same value in two coexistent phases, but the ratios of the quantities η, v, m_1, m_2,

$\ldots m_n$ are in general different in the two phases. Or, if for convenience we compare equal volumes of the two phases (which involves no loss of generality), the quantities η, m_1, m_2, $\ldots m_n$ will in general have different values in two coexistent phases. Applying this to coexistent phases indefinitely near to a critical phase, . . . if the values of n of the quantities t, p, μ_1, μ_2, $\ldots \mu_n$ are regarded as constant (as well as v),* the variations of either of the others will be infinitely small compared with the variations of the quantities η, m_1, m_2, $\ldots m_n$. This condition, which we may write in the form

$$\left(\frac{d\mu_n}{dm_n}\right)_{t,\, v,\, \mu_1,\, \ldots\, \mu_{n-1}} = 0, \qquad (242)\ [200]$$

characterizes . . . the limits which divide stable from unstable phases with respect to continuous changes."

Critical phases are also at the limit which divides stable from unstable phases in respect to discontinuous changes. Thus, in Figure 8, phases represented by points inside the curve *ACB* are unstable with regard to the formation of the coexistent phases, represented by points on this curve. The coexistent phases thus lie on the limit which separates stable from unstable phases in respect to discontinuous changes, and the same must be true of the critical phase.

The series of phases determined by giving t and p the constant values which they have in the coexistent phases N and P (Fig. 8) consists of unstable phases in the part NP between the coexistent phases, but in the parts MN and PQ, beyond these phases, it consists of stable phases. But when t and p are given the constant values determined by the critical phase C, the whole series of phases XY (obtained by varying the composition) is stable. Thus, in general, "if a critical phase is varied in such a manner that n of the quantities t, p, μ_1, μ_2, $\ldots \mu_n$ remain constant, it will remain stable in respect both to continuous and to discontinuous changes. Therefore, μ_n is an increasing function of m_n when $t, v, \mu_1, \mu_2, \ldots \mu_{n-1}$ have constant values* determined by any critical phase." If

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* Since two coexistent phases are only capable of n independent variations, this condition ensures that the variation considered corresponds to the change from one coexistent state to the other, which is infinitely close to it.

$$(d^2\mu_n/dm_n^{\,2})_{t,\,v,\,\mu_1,\,\ldots\,\mu_{n-1}}$$

had either a positive or a negative value, μ_n would be a maximum or a minimum with respect to m_n, at the critical point, when (242) is satisfied. Thus, since μ_n is an increasing function of m_n, we have

$$\left(\frac{d^2\mu_n}{dm_n^{\,2}}\right)_{t,\,v,\mu_1,\,\mu_2,\,\ldots\,\mu_{n-1}} = 0, \qquad (243)\ [201]$$

but one of the higher differentials must be positive, i.e.,

$$\left(\frac{d^3\mu_n}{dm_n^{\,3}}\right)_{t,\,v,\,\mu_1,\,\mu_2,\,\ldots\,\mu_{n-1}} \geqq 0, \text{ etc.} \qquad (244)\ [202]$$

XII. Generalized Conditions of Stability†

37. The Conditions. A single phase of n components has $n + 1$ degrees of freedom. Therefore, if n of the quantities $t, p, \mu_1, \ldots \mu_n$ are given constant values, the phase is only capable of one independent variation. If we take $\eta, v_1, m_1, \ldots m_n$ as the independent variables, we may write (when $dv = 0$)

$$\left.\begin{aligned} dt &= \frac{dt}{d\eta}\,d\eta + \frac{dt}{dm_1}\,dm_1 \ldots + \frac{dt}{dm_n}\,dm_n, \\ d\mu_1 &= \frac{d\mu_1}{d\eta}\,d\eta + \frac{d\mu_1}{dm_1}\,dm_1 \ldots + \frac{d\mu_1}{dm_n}\,dm_n, \\ &\cdot\quad\cdot\quad\cdot\qquad\qquad\cdot\quad\cdot\quad\cdot \\ d\mu_n &= \frac{d\mu_n}{d\eta}\,d\eta + \frac{d\mu_n}{dm_1}\,dm_1 \ldots + \frac{d\mu_n}{dm_n}\,dm_n. \end{aligned}\right\} \qquad (245)\ [172]$$

When $dt = 0, d\mu_1 = 0, \ldots d\mu_{n-1} = 0$, we have

$$\left(\frac{d\mu_n}{dm_n}\right)_{t,\,v,\,\mu_1,\,\ldots\,\mu_{n-1}} = \frac{R_{n+1}}{R_n}, \qquad (246)\ [175]$$

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* v is included to insure that a change in the *amount* of the critical phase is excluded.

† Gibbs, I, 111–112.

where R_{n+1} is the determinant,

$$\begin{vmatrix} \dfrac{d^2\epsilon}{d\eta^2} & \dfrac{d^2\epsilon}{dm_1 d\eta} & \cdots & \dfrac{d^2\epsilon}{dm_n d\eta} \\ \dfrac{d^2\epsilon}{d\eta dm_1} & \dfrac{d^2\epsilon}{dm_1^2} & \cdots & \dfrac{d^2\epsilon}{dm_n dm_1} \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{d^2\epsilon}{d\eta dm_n} & \dfrac{d^2\epsilon}{dm_1 dm_n} & \cdots & \dfrac{d^2\epsilon}{dm_n^2} \end{vmatrix}, \qquad (247)\ [173]$$

the constituents of which, by (44), are the same as the coefficients of the equations (245), (thus $dt/d\eta = d^2\epsilon/d\eta^2$, $d\mu_n/dm_n = d^2\epsilon/dm_n^2$, etc.) and R_n is the determinant formed by erasing the last row and column of R_{n+1}. Similarly, the determinants R_{n-1}, R_{n-2}, etc., are obtained by erasing successively the last row and column of R_n, and

$$\left(\frac{d\mu_{n-1}}{dm_{n-1}}\right)_{t,\, v,\, \mu_1, \ldots \mu_{n-2},\, \mu_n} = \frac{R_n}{R_{n-1}}, \text{ etc.} \qquad (248)\ [176]$$

Now according to (230) and (232) the phase is stable if the differential coefficients (246), (248), etc. are all positive. These conditions are satisfied if the determinant (247) and all its minors, down to $d^2\epsilon/d\eta^2$, are positive.* "Any phase for which this condition is satisfied will be stable, and no phase will be stable for which any of these quantities has a negative value." Since the conditions (230) remain valid if we replace any of the subscript μ's by m's, the order in which we erase the successive columns with the corresponding rows in the determinant is immaterial.

For a body of invariable composition, it is only necessary to use the terms which are common to the first two rows and columns of (245) and (247). But in this case it is more convenient to make $dm = 0$. Then we may write

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* The differential coefficients in (246), (248), etc. would also be positive if *all* the determinants, R_{n+1}, R_n, etc. were negative. But the last term $d^2\epsilon/d\eta^2$, by (229), cannot be negative, so none of the others can be negative.

$$\left.\begin{aligned} dt &= \frac{dt}{d\eta}\,d\eta + \frac{dt}{dv}\,dv, \\ dp &= \frac{dp}{d\eta}\,d\eta + \frac{dp}{dv}\,dv; \end{aligned}\right\} \tag{249}$$

and, when $dt = 0$, the value of dp/dv is given by

$$\begin{vmatrix} \dfrac{d^2\epsilon}{d\eta^2} & \dfrac{d^2\epsilon}{d\eta dv} \\ -\dfrac{d^2\epsilon}{dv d\eta} & -\dfrac{d^2\epsilon}{dv^2} \end{vmatrix} \tag{250}$$

since, by (44), $t = (d\epsilon/d\eta)_{v,m}$ and $p = -(d\epsilon/dv)_{t,m}$. In stable phases, $(dp/dv)_{t,m}$ must be negative. Thus, expanding (250), a phase of invariable composition is stable when

$$\frac{d^2\epsilon}{d\eta^2}\cdot\frac{d^2\epsilon}{dv^2} - \left(\frac{d^2\epsilon}{d\eta dv}\right)^2 > 0, \qquad \frac{d^2\epsilon}{d\eta^2} > 0. \tag{251}$$

The physical meaning of these conditions can be seen from a consideration of the η–v–ϵ surface for homogeneous phases. Let η, v, ϵ be the coordinates on this surface of the point D, representing the phase in question. Let E be the neighbouring point on the surface, with coordinates $\eta + \Delta\eta$, $v + \Delta v$, $\epsilon + \Delta\epsilon$, and E' the point of intersection of the tangent plane through D with the vertical erected at E. (See Fig. 6.) Let the ordinate of E' be $\epsilon + \Delta\epsilon'$. Then, to the second order of small quantities,

$$\Delta\epsilon = \frac{d\epsilon}{d\eta}\,\Delta\eta + \frac{d\epsilon}{dv}\,\Delta v + \tfrac{1}{2}\,\frac{d^2\epsilon}{d\eta^2}\,\Delta\eta^2 + \frac{d^2\epsilon}{d\eta dv}\,\Delta\eta\Delta v + \tfrac{1}{2}\,\frac{d^2\epsilon}{dv^2}\,\Delta v^2,$$

and

$$\Delta\epsilon' = \frac{d\epsilon}{d\eta}\,\Delta\eta + \frac{d\epsilon}{dv}\,\Delta v$$

(since $d\epsilon/d\eta$, $d\epsilon/dv$ define the slope of the tangent plane at D). Thus

$$EE' = \Delta\epsilon - \Delta\epsilon'$$

$$= \tfrac{1}{2}\frac{d^2\epsilon}{d\eta^2}\Delta\eta^2 + \frac{d^2\epsilon}{d\eta dv}\Delta\eta\Delta v + \tfrac{1}{2}\frac{d^2\epsilon}{dv^2}\Delta v^2.$$

The expression on the right of this equation is positive when

$$\frac{d^2\epsilon}{d\eta^2}\cdot\frac{d^2\epsilon}{dv^2} - \left(\frac{d^2\epsilon}{d\eta dv}\right)^2 > 0, \qquad \frac{d^2\epsilon}{d\eta^2} > 0, \qquad \text{and } \frac{d^2\epsilon}{dv^2} > 0,$$

(the last condition is a consequence of the other two), so that when these conditions are fulfilled E lies above E'. Thus the conditions which were obtained above signify that a phase is stable with respect to continuous changes, when the η-v-ϵ surface for adjacent phases lies above the tangential plane at the point representing the phase in question, except at the single point of contact.

It is often more convenient to use other sets of quantities as the independent variables. Thus if we employ t, v, m_1, m_2, $\ldots m_n$ as independent variables, we have when $dt = 0$ and $dm_n = 0$,*

$$\left.\begin{aligned} dp &= \frac{dp}{dv}dv + \frac{dp}{dm_1}dm_1 \ldots + \frac{dp}{dm_{n-1}}dm_{n-1}, \\ d\mu_1 &= \frac{d\mu_1}{dv}dv + \frac{d\mu_1}{dm_1}dm_1 \ldots + \frac{d\mu_1}{dm_{n-1}}dm_{n-1}, \\ &\cdot \quad \cdot \quad \cdot \qquad\qquad\qquad \cdot \quad \cdot \quad \cdot \\ d\mu_{n-1} &= \frac{d\mu_{n-1}}{dv}dv + \frac{d\mu_{n-1}}{dm_1}dm_1 \ldots + \frac{d\mu_{n-1}}{dm_{n-1}}dm_{n-1}; \end{aligned}\right\} \quad (252)$$

whence, when $dt = 0$, $dp = 0$, $d\mu_1 = 0$, $\ldots d\mu_{n-2} = 0$,

$$\left(\frac{d\mu_{n-1}}{dm_{n-1}}\right)_{t,\, p,\, \mu_1, \ldots \mu_{n-2},\, m_n} = \frac{P_n}{P_{n-1}}, \qquad (253)$$

---

* In order that every variation considered shall represent a real change of phase, it is necessary to make one of the quantities v, m_1, m_2, $\ldots m_n$ constant.

where, by (45),

$$P_n = \begin{vmatrix} -\dfrac{d^2\psi}{dv^2} & -\dfrac{d^2\psi}{dvdm_1} & \cdots & -\dfrac{d^2\psi}{dvdm_{n-1}} \\ \dfrac{d^2\psi}{dm_1dv} & \dfrac{d^2\psi}{dm_1^2} & \cdots & \dfrac{d^2\psi}{dm_1dm_{n-1}} \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{d^2\psi}{dm_{n-1}dv} & \dfrac{d^2\psi}{dm_{n-1}dm_1} & \cdots & \dfrac{d^2\psi}{dm_{n-1}^2} \end{vmatrix}, \tag{254}$$

and the determinants P_{n-1}, etc. are obtained by erasing successively the last row and the corresponding column in (254). By (231), dp/dv or $(-d^2\psi/dv^2)$ cannot be positive for a stable phase, therefore none of the determinants derived from (254) can be positive. If they are all negative the phase is necessarily stable. For two components, when $dm_2 = 0$, these conditions become

$$\frac{d^2\psi}{dv^2}\cdot\frac{d^2\psi}{dm_1^2} - \left(\frac{d^2\psi}{dvdm_1}\right)^2 > 0, \qquad \frac{d^2\psi}{dv^2} > 0, \qquad \frac{d^2\psi}{dm_1^2} > 0, \tag{255}$$

the last of which is a consequence of the other two. Thus, if we construct a surface, the points of which have as coordinates the values of v_1, m_1, ψ for homogeneous phases having the same temperature and a constant value of m_2, the condition of stability of any phase is that the surface shall be above the tangent plane taken at the point representing this phase, for all adjacent phases.

Lastly, if t, p, m_1, $m_2, \ldots m_n$ are taken as the independent variables, and $dt = 0$, $dp = 0$, and $dm_n = 0$, we have

$$\left.\begin{aligned} d\mu_1 &= \frac{d\mu_1}{dm_1}dm_1 + \frac{d\mu_1}{dm_2}dm_2 \ldots + \frac{d\mu_1}{dm_{n-1}}dm_{n-1}, \\ d\mu_2 &= \frac{d\mu_2}{dm_1}dm_1 + \frac{d\mu_2}{dm_2}dm_2 \ldots + \frac{d\mu_2}{dm_{n-1}}dm_{n-1}, \\ &\cdot \quad \cdot \quad \cdot \qquad\qquad \cdot \quad \cdot \quad \cdot \\ d\mu_{n-1} &= \frac{d\mu_{n-1}}{dm_1}dm_1 + \frac{d\mu_{n-1}}{dm_2}dm_2 \ldots + \frac{d\mu_{n-1}}{dm_{n-1}}dm_{n-1}. \end{aligned}\right\} \tag{256}$$

Therefore, by (43),

$$\left(\frac{d\mu_{n-1}}{dm_{n-1}}\right)_{t,\,p,\,\mu_1,\,\ldots\,\mu_{n-2},\,m_n} = \frac{U_{n-1}}{U_{n-2}}, \tag{257}$$

where U_{n-1} is the determinant

$$\begin{vmatrix} \dfrac{d^2\zeta}{dm_1^2} & \dfrac{d^2\zeta}{dm_1\,dm_2} & \cdots & \dfrac{d^2\zeta}{dm_1\,dm_{n-1}} \\ \dfrac{d^2\zeta}{dm_2\,dm_1} & \dfrac{d^2\zeta}{dm_2^2} & \cdots & \dfrac{d^2\zeta}{dm_2\,dm_{n-1}} \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{d^2\zeta}{dm_{n-1}\,dm_1} & \dfrac{d^2\zeta}{dm_{n-1}\,dm_2} & \cdots & \dfrac{d^2\zeta}{dm_{n-1}^2} \end{vmatrix}, \tag{258) [206}$$

and U_{n-2}, etc. are the minors obtained by erasing successively the last column and the corresponding row. A phase for which all these determinants have positive values is therefore stable.

When there are three components and $dm_3 = 0$, these conditions become

$$\frac{d^2\zeta}{dm_1^2}\cdot\frac{d^2\zeta}{dm_2^2} - \left(\frac{d^2\zeta}{dm_1\,dm_2}\right)^2 > 0, \qquad \frac{d^2\zeta}{dm_1^2} > 0,$$

$$\frac{d^2\zeta}{dm_2^2} > 0. \tag{259}$$

If, instead of making m_3 constant, we use as the variables expressing the composition $x = m_1/(m_1 + m_2 + m_3)$ and $y = m_2/(m_1 + m_2 + m_3)$, these conditions may be obtained in the form

$$\frac{d^2\zeta}{dx^2}\cdot\frac{d^2\zeta}{dy^2} - \left(\frac{d^2\zeta}{dx\,dy}\right)^2 > 0, \qquad \frac{d^2\zeta}{dx^2} > 0, \qquad \frac{d^2\zeta}{dy^2} > 0. \tag{260}$$

Thus if a ζ-surface is constructed for homogeneous phases having the same temperature and pressure, with coordinates x, y, ζ, the condition of stability of any phase is that the ζ-surface for adjacent phases shall be above the tangent plane, taken at the point representing the phase in question, everywhere except at the single point of contact.

In general the condition of the limit of stability is represented by substituting = for > in any of these equations.

*38. Critical Phases.** Since a critical phase may be varied without changing any of the quantities t, μ_1, μ_2, $\ldots \mu_n$, all the expressions (245) may be equated to zero. The solution of the equations so obtained is

$$R_{n+1} = 0. \qquad (261)\ [203]$$

(This also follows from the fact that a critical phase is at the limit of stability with respect to continuous changes.) "To obtain the second equation characteristic of critical phases, we observe that as a phase which is critical cannot become unstable when varied so that n of the quantities t, p, μ_1, $\mu_2, \ldots \mu_n$ remain constant, the differential of R_{n+1} for constant volume, viz.,

$$\frac{d\,R_{n+1}}{d\eta}\,d\eta + \frac{d\,R_{n+1}}{dm_1}\,dm_1 \ldots + \frac{d\,R_{n+1}}{dm_n}\,dm_n \qquad (262)\ [204]$$

cannot become negative" when n of the quantities t, p, μ_1, μ_2, $\ldots \mu_n$ remain constant. "Neither can it have a positive value, for then its value might become negative by a change of sign of $d\eta$, dm_1, etc." Therefore the expression (262) has the value zero, when n of the expressions (245) are equated to zero. If S is a determinant in which the constituents are the same as in R_{n+1} except that the differential coefficients

$$\frac{dR_{n+1}}{d\eta},\ \frac{dR_{n+1}}{dm_1},\ \ldots\ \frac{dR_{n+1}}{dm_n} \qquad (263)$$

are substituted in a single horizontal line, this condition is expressed by the equation

$$S = 0. \qquad (264)\ [205]$$

This substitution may be made in any horizontal line of R_{n+1}.

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* Gibbs, I, 132–134.

These conditions may be expressed in terms of other sets of variables. Thus using the variables of (252), we have

$$P_n = 0, \qquad \text{and} \qquad Q_n = 0, \tag{265}$$

where Q_n is the determinant formed by substituting the coefficients

$$\frac{dP_n}{dv}, \frac{dP_n}{dm_1}, \dots \frac{dP_n}{dm_{n-1}} \tag{266}$$

in any line of (254). For a system of one component, these equations become

$$\left(\frac{d^2\psi}{dv^2}\right)_{t,\,m} = 0, \qquad \left(\frac{d^3\psi}{dv^3}\right)_{t,\,m} = 0. \tag{267}$$

Again, using the variables in (256), we have as the equations of critical phases,

$$U_{n-1} = 0, \qquad \text{and} \qquad V_{n-1} = 0, \qquad (268)\ [208]$$

where V_{n-1} is the determinant formed by substituting the coefficients

$$\frac{dU_{n-1}}{dm_1}, \frac{dU_{n-1}}{dm_2}, \dots \frac{dU_{n-1}}{dm_{n-1}} \qquad (269)\ [207]$$

in any line of (258). For two components, these equations become

$$\left(\frac{d^2\zeta}{dm_1^2}\right)_{t,\,p,\,m_2} = 0, \qquad \left(\frac{d^3\zeta}{dm_1^3}\right)_{t,\,p,\,m_2} = 0. \tag{270}$$

Instead of making m_2 constant, we may use as the variable expressing the composition, $x = m_1/(m_1 + m_2)$. Then we have as the equations of a critical phase

$$\left(\frac{d^2\zeta}{dx^2}\right)_{t,\,p} = 0, \qquad \left(\frac{d^3\zeta}{dx^3}\right)_{t,\,p} = 0. \tag{271}$$

As an illustration of these relations we will return to a consideration of the ζ-composition diagram of a two component system. Suppose that at a pressure p and a temperature t', the ζ-x curve for homogeneous phases has the form AB (Fig. 9), with a double tangent PQ. Homogeneous phases between P and Q are unstable with respect to discontinuous changes. Between R and S, the ζ-curve is convex upwards, i.e.,

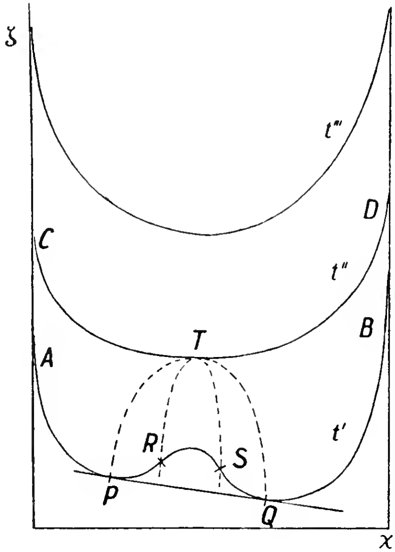

FIG. 9

$$(d^2\zeta/dx^2)_{p,\,t} < 0,$$

and these phases are unstable with respect to continuous changes. Between P and R, and between Q and S the ζ-curve is still concave upwards, i.e.,

$$(d^2\zeta/dx^2)_{p,\,t} > 0,$$

and these phases, though unstable with regard to discontinuous changes are stable with regard to continuous changes. The points R and S, for which

$$d^2\zeta/dx^2 = 0,$$

thus represent the limits of stability with regard to continuous changes. If the temperature is varied in the direction of the critical point, the phases P and Q approach each other and at the critical temperature become identical. If CD is the ζ-curve at the critical temperature t'', the point T representing the critical phase, where the points P, Q, R, S, all coalesce, is a point of undulation at which

$$(d^2\zeta/dx^2)_{p,\,t} = 0 \quad \text{and} \quad (d^3\zeta/dx^3)_{p,\,t} = 0.$$

Finally, at a temperature t''' beyond the critical point, the ζ-curve is concave everywhere. Now $(d^2\zeta/dx^2)_{t,\,p}$ is positive for all homogeneous phases, which are stable with regard to both continuous and discontinuous changes.

It is evident that by a slight variation of the critical phase we may obtain either (1), a phase which is unstable with regard to both continuous or discontinuous changes, or (2), a phase which is stable with regard to continuous changes but unstable with regard to discontinuous changes, or (3), a phase which is stable with regard to both continuous and discontinuous changes.

XIII. Equilibrium of Two Components in Two Phases

39. The Equilibrium. We can now consider in more detail the relation between temperature, pressure and composition in systems of two components, S_1 and S_2, in two phases. Let the quantities referring to the first phase be distinguished by single accents, and those referring to the second phase by double accents. Then, for any change of state, while the phases remain in equilibrium, we have

$$\left.\begin{aligned} v'\,dp &= \eta'\,dt + m_1'\,d\mu_1 + m_2'\,d\mu_2, \\ v''dp &= \eta''dt + m_1''d\mu_1 + m_2''d\mu_2. \end{aligned}\right\} \qquad (272)$$

If we consider quantities of the phases for which $m_2' = m_2''$, we have

$$(v'' - v')dp = (\eta'' - \eta')dt + (m_1'' - m_1')d\mu_1. \qquad (273)$$

Now, we may express $d\mu_1$ as a function of p, t, m_1 by the equation

$$d\mu_1 = \left(\frac{d\mu_1}{dp}\right)_{t,\,m} dp + \left(\frac{d\mu_1}{dt}\right)_{p,\,m} dt + \left(\frac{d\mu_1}{dm_1}\right)_{p,\,t,\,m_2} dm_1. \quad (274)$$

This equation may be applied to either of the two phases. Applying it to the first phase, we may write, by (158) and (159),

$$\left(\frac{d\mu_1}{dp}\right)'_{t,\,m} = \bar{v}_1{}', \qquad \left(\frac{d\mu_1}{dt}\right)'_{p,\,m} = -\,\bar{\eta}_1{}'.$$

Hence, substituting in (273) the value of $d\mu$ given by these equations and rearranging, we find

$$\begin{aligned}&[(v'' - v') - (m_1{}'' - m_1{}')\,\bar{v}_1{}']\,dp\\ &= [(\eta'' - \eta') - (m_1{}'' - m_1{}')\,\bar{\eta}_1{}']\,dt\\ &+ (m_1{}'' - m_1{}')\left(\frac{d\mu_1}{dm_1}\right)'_{p,\,t,\,m_2} \cdot dm_1{}'. \end{aligned} \quad (275)$$

Similarly, when the terms of (274) are determined by the second phase, we obtain

$$\begin{aligned}&[(v'' - v') - (m_1{}'' - m_1{}')\,\bar{v}_1{}'']\,dp\\ &= [(\eta'' - \eta') - (m_1{}'' - m_1{}')\,\bar{\eta}_1{}'']\,dt\\ &+ (m_1{}'' - m_1{}')\left(\frac{d\mu_1}{dm_1}\right)''_{p,\,t,\,m_2} \cdot dm_1{}''. \end{aligned} \quad (276)$$

In order to interpret these equations we may first observe that v' is the volume of the quantity of the first phase which contains $m_1{}'$ of the first component. Thus $[v' + (m_1{}'' - m_1{}')\,(dv'/dm_1{}')]$ is approximately equal to the volume of that quantity of this phase which contains $m_1{}''$ of this substance. Hence we see that $[v'' - v' - (m_1{}'' - m_1{}')\,\bar{v}_1{}']$ is approximately equal to the difference of the volumes of quantities of the two phases containing the same amount (viz., $m_1{}''$) of this substance. In the same way $[v'' - v' - (m_1{}'' - m_1{}')\bar{v}_1{}'']$ is the approximate difference of volume of quantities of the two phases which contain the same amount (m_1') of this component. The terms relating to the entropy can be interpreted in a similar way. Secondly, by (253) or (257) the differential coefficient $(d\mu_1/dm_1)_{t,\ p,\ m_2}$ is positive in both phases.*

40. Konowalow's Laws. In the case in which the first phase is liquid and the second a gaseous phase, the coefficients of dp in (275) and (276) are evidently positive. Then, when $dt = 0$, we see that

(1) From (275), dp has the same sign as $(m_1'' - m_1')\ dm_1'$, and from (276), dp has the same sign as $(m_1'' - m_1')\ dm_1''$. Therefore dm_1' has the same sign as dm_1''.

(2) Since dp has the same sign as $(m_1'' - m_1')\ dm_1'$, dp and dm_1' have the same sign if $m_1'' > m_1'$, and opposite signs if $m_1'' < m_1'$.

Thus we may draw the following conclusions:

(1) When the composition of the liquid phase is changed, that of the vapor phase changes in the same sense.

(2) If the proportion of S_1 is greater in the vapor than in the liquid phase, when the temperature remains constant the pressure is increased by the addition of S_1.

In the same way, it can easily be shown that when $dp = 0$, dt and dm_1' have opposite signs when $m_1'' > m_1'$. Therefore we have

(3) If the proportion of S_1 is greater in the vapor than in the liquid phase, when the pressure remains constant the temperature is decreased by the addition of S_1.

(4) If the proportion of S_1 is the same in the vapor as in the liquid phase, the pressure is a maximum or a minimum at constant temperature, and the temperature a maximum or minimum at constant pressure (See p. 113).

These rules, which are illustrated by the examples shown in Figures 2 and 3, were first stated by D. Konowalow.†

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* It may be zero if the phase is at the limit of stability.

† *Wied. Annalen,* 14, 48 (1881).

XIV. Phases of Dissipated Energy. Catalysis*

41. Dissipated Energy. In considering the conditions of equilibrium of heterogeneous masses, changes which are "prevented by passive forces or analogous resistances to change" have been excluded. Thus it often happens that "the number of proximate components which it is necessary to recognise as independently variable in a body exceeds the number of components which would be sufficient to express its composition." Thus, at low temperatures the combination of hydrogen and oxygen may be regarded as prevented by passive forces, and in a system containing hydrogen, oxygen and water it is necessary to recognize all three substances as independently variable components.

At higher temperatures, when the combination of hydrogen and oxygen is not prevented by passive forces, the state of the system is entirely determined by the temperature, pressure and the total quantities of hydrogen and oxygen present. The value of ζ can be expressed as a function of these four variables. The fact that part of the matter present exists in the form of water vapour does not affect the form of this function, but it is one of the facts which determine the nature of the relation between ζ and the above mentioned variables.

In cases like those first mentioned, of all the phases which may be formed from the given matter, there are some for which the energy is as small as that of any other state of the same matter having the same entropy and volume, or for which the value of ζ is as small as that of any other state of the same matter at the same temperature and pressure. These are called phases of dissipated energy.

It is characteristic of such phases that the equilibrium can only be slightly disturbed by the action of a small body, or by the action of a single electric spark. The effect produced by any such action is in some way proportionate to its cause. But in a phase which is not a phase of dissipated energy, it may be possible to cause very great changes by contact with a very small body, or other action. Such changes may only be limited by the attainment of a phase of dissipated energy.

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* Gibbs, I, 138–141.

Gibbs describes the effects which may cause a system to undergo changes of this kind in the following terms:

"Such a result will probably be produced in a fluid mass by contact with another fluid which contains molecules of all the kinds which occur in the first fluid (or at least all those which contain the same kinds of matter which also occur in other sorts of molecules), but which differs from the first fluid in that the quantities of the various kinds of molecules are entirely determined by the ultimate composition of the fluid and its temperature and pressure. Or, to speak without reference to the molecular state of the fluid, the result considered would doubtless be brought about by contact with another fluid, which absorbs all the proximate components of the first, $S_1, \ldots S_n$, independently, and without passive resistances, but for which the phase is completely determined by its temperature and pressure and its ultimate composition (in respect at least to the particular substances just mentioned). By the absorption of the substances $S_1, \ldots S_n$ independently and without passive resistances, it is meant that when the absorbing body is in equilibrium with another containing these substances, it shall be possible by *infinitesimal* changes in these bodies to produce the exchange of all these substances in either direction and independently. An exception to the preceding statement may of course be made for cases in which the result in question is prevented by the occurrence of some other kinds of change; in other words, it is assumed that the two bodies can remain in contact preserving the properties which have been mentioned.

"The term *catalysis* has been applied to such action as we are considering. When a body has the property of reducing another, without limitation with respect to the proportion of the two bodies, to a phase of dissipated energy, in regard to a certain kind of molecular change, it may be called a *perfect catalytic agent* with respect to the second body and the kind of molecular change considered."

E

OSMOTIC AND MEMBRANE EQUILIBRIA, INCLUDING ELECTROCHEMICAL SYSTEMS

[Gibbs, I, pp. 83–85; 413–417]

E. A. GUGGENHEIM

1. Introduction. The power and elegance of the methods of Willard Gibbs in thermodynamics are nowhere better illustrated than in their application to membrane equilibria.* Owing to the form in which he expressed the conditions for chemical equilibria, the same conditions for the equilibrium between two phases as regards a given species hold good whether the two

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* A list of the most important symbols used, in addition to those used by Gibbs, is as follows:

E	Electromotive force of cell.
F	Faraday.
f_i	Activity coefficient of species S_i.
$f_\pm$	Mean activity coefficient of electrolyte.
g	Osmotic coefficient.
N_i	Mol fraction of species S_i.
P	Osmotic pressure.
q_+, q_-	Number of cations and anions per mol of electrolyte.
r	Ratio of partial molar volume at infinite dilution of electrolyte to that of solvent, both at a pressure equal to the mean of those at either side of membrane.
v_i	Partial molar volume of species S_i at given temperature, pressure and composition.
v_i^*	Partial molar volume of species S_i at given temperature, zero pressure and infinite dilution.
$[v_i]$	Partial molar volume of species S_i at given temperature, infinite dilution and at a pressure equal to the mean of those at either side of the membrane.
z_i	Valency, positive or negative, of ionic species S_i.
κ_i	Coefficient of compressibility of species S_i at infinite dilution.
$[\mu_i]$	Potential of ionic species S_i.

The suffix 0 always refers to the solvent species, e.g., v_0^* is the molar volume of the pure solvent at zero pressure.

phases be in complete equilibrium or only in partial equilibrium, that is, in equilibrium as regards this species but not as regards all the species present.

The general conditions that two phases, denoted respectively by a single and by a double accent, shall be in complete equilibrium are the following. First, in order that the two phases shall be in thermal equilibrium the temperatures of the two phases must be the same, that is,

$$t' = t''. \qquad (1)\ [19]$$

Second, in order that the two phases shall be in mechanical or hydrostatic equilibrium the pressures of the two phases must be equal, or

$$p' = p''. \qquad (2)\ [20]$$

Third, in order that the two phases shall be in chemical equilibrium as regards the various chemical species $S_1, S_2, \ldots S_n$ the potential of each species must be the same in the two phases, or

$$\left.\begin{array}{l} \mu_1' = \mu_1'', \\ \mu_2' = \mu_2'', \\ \dots\dots\dots \\ \mu_n' = \mu_n''. \end{array}\right\} \qquad (3)\ [21]$$

The essential feature of Gibbs' treatment of equilibrium is that, thanks to his invention of the potentials of the chemical species, the conditions (3) [21] for chemical equilibrium are of a form analogous to the condition (1) [19] for thermal equilibrium and to the condition (2) [20] for hydrostatic equilibrium.

The importance and usefulness of Gibbs' method for the treatment of membrane equilibria depend on the fact that, provided two phases are in thermal equilibrium, i.e., (1) [19] is satisfied, the other equilibrium conditions, namely, (2) [20] for hydrostatic equilibrium and the several equations of (3) [21] for chemical equilibrium, are all independent of one another. In other words, if two phases, denoted respectively by a single and by a double accent, be separated by a membrane capable of supporting an excess of pressure on either side and permeable to some of the components S_h, S_i, ..., but impermeable to others S_a, S_b, ..., the conditions for equilibrium between the two phases as regards the components S_h, S_i, ...,

$$\left.\begin{array}{l} \mu_h' = \mu_h'', \\ \mu_i' = \mu_i'', \\ \dots\dots\dots \end{array}\right\} \qquad (4)\ [77]$$

are of exactly the same form as (3) [21].

But the potentials of the components S_a, S_b, ..., to which the membrane is impermeable, will in general not be equal, that is,

$$\left.\begin{array}{l} \mu_a' \neq \mu_a'', \\ \mu_b' \neq \mu_b'', \\ \dots\dots\dots \end{array}\right\} \qquad (5)\ [77]$$

Moreover, in general the pressures of the two phases will not be equal, that is,

$$p' \neq p''. \qquad (6)\ [77]$$

The pressure on each phase will be equal and opposite to the pressure exerted by the phase on the membrane, and so the resultant force per unit area on the membrane will be equal to the difference between the pressures of the two phases.

2. Proof of General Conditions of Membrane Equilibrium. The derivation of the general conditions (4) [77] of membrane equilibrium is given by Gibbs (I, 83). In this proof the quantities chosen as independent variables are the entropy η of each phase, the volume v of each phase, and the quantities m_1, m_2, ... m_n of the various chemical species S_1, S_2, ... S_n in each phase. The corresponding characteristic function is the energy ϵ. The appropriate form for the general criterion of the equilibrium is that expressed by [2] (Gibbs, I, 56).

In accordance with the footnote (Gibbs, I, 90) a somewhat more familiar derivation of (4) [77] can be obtained by choosing as independent variable the temperature t instead of the entropy

η of each phase and by taking for granted the condition for thermal equilibrium (1) [19].

With this choice of independent variables the characteristic function is ψ defined by

$$\psi = \epsilon - t\eta. \tag*{(7) [87]}$$

Its dependence on the independent variables t, v, m_1, m_2, ... m_n is given by

$$d\psi = -\eta dt - pdv + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n. \tag*{(8) [88]}$$

The condition of membrane equilibrium takes the form

$$d\psi' + d\psi'' = 0, \tag*{(9.1) [111]}$$

subject to

$$dt' = dt'' = 0, \tag*{(9.2)}$$

$$dv' = dv'' = 0, \tag*{(9.3) [73]}$$

$$\left.\begin{array}{l} dm_a' = dm_a'' = 0, \\ dm_b' = dm_b'' = 0, \\ \dots\dots\dots\dots\dots\dots \end{array}\right\} \tag*{(9.4) [74]}$$

$$\left.\begin{array}{l} dm_h' + dm_h'' = 0, \\ dm_i' + dm_i'' = 0, \\ \dots\dots\dots\dots\dots\dots \end{array}\right\} \tag*{(9.5) [75]}$$

Substituting from (8) into (9.1), and using (9.2), (9.3), (9.4) and (9.5), we obtain

$$(\mu_h' - \mu_h'')dm_h' + (\mu_i' - \mu_i'')dm_i' + \dots = 0. \tag*{(10)}$$

If m_h', m_i', ... are independently variable it follows that

$$\left.\begin{array}{l} \mu_h' = \mu_h'', \\ \mu_i' = \mu_i'', \\ \dots\dots\dots \end{array}\right\} \tag*{(11) [77]}$$

The same form, (11) [77], for the conditions of membrane equilibrium is thus obtained whether entropy or temperature be chosen as one of the independent variables. In fact, whatever choice one makes of independent variables an analogous treatment will lead to the same result, (11) [77].

3. Choice of Independent Components. If the various quantities $m_h, m_i, \ldots$ are not independently variable but are subject to certain restrictions expressible in the form of linear relations between $dm_h, dm_i, \ldots$, then (10) holds not for any values of $dm_h, dm_i, \ldots$ but only for such sets of values of $dm_h, dm_i, \ldots$ as conform with the linear restrictions. Instead of the conditions (11) [77] one then obtains a smaller number of independent conditions of the type [78] (Gibbs, I, 83). The physical meaning of this is quite simple. The condition for membrane equilibrium is equality of the potential for those components to which the membrane is permeable, provided the species chosen as independent components include all those which are able to pass the membrane independently. An example will make this clear. Suppose the membrane is permeable to methyl alcohol CH_4O but not to water H_2O. Then the corresponding condition of membrane equilibrium is

$$\mu'_{CH_4O} = \mu''_{CH_4O}. \tag{12}$$

But from a purely thermodynamic standpoint it would be allowable to choose as independent components methylene CH_2 and water H_2O, since these will serve just as well as methyl alcohol CH_4O and water H_2O to define the composition of each phase. With this choice of components both methylene and water are able to pass through the membrane, not independently but only in the proportions in which they form methyl alcohol. Formula (10) in this case is

$$(\mu'_{CH_2} - \mu''_{CH_2})\, dm'_{CH_2} + (\mu'_{H_2O} - \mu''_{H_2O})\, dm'_{H_2O} = 0. \tag{13}$$

But dm_{CH_2} and dm_{H_2O} are subject to the restriction

$$\frac{dm_{CH_2}}{p} = \frac{dm_{H_2O}}{q}, \tag{14}$$

where p/q is the ratio in which methylene and water combine to form methyl alcohol. Substituting (14) into (13) we obtain

$$p\mu'_{CH_2} + q\mu'_{H_2O} = p\mu''_{CH_2} + q\mu''_{H_2O}. \tag{15}$$

But according to [121] and the definition of the ratio it follows that (15) is equivalent to

$$\mu'_{CH_4O} = \mu''_{CH_4O}, \tag{16}$$

the same as (12). We see then that the complications discussed by Gibbs in the paragraph preceding [78] can be avoided if we always include among the independent components all those species which can pass through the membrane independently.

4. Choice of Independent Variables. Although the conditions for any membrane equilibria are completely contained in Gibbs' formula [77] it is advantageous from a practical point of view to transform this into a form involving quantities more directly measurable than the potential μ. For this purpose it is most convenient to choose as independent variables the temperature t, the pressure p and the number $m_1, m_2, \ldots m_n$ of units of quantity of the various species $S_1, S_2, \ldots S_n$. The potentials $\mu_1, \mu_2, \ldots \mu_n$ in each phase will then be regarded as functions of $t, p, m_1, m_2, \ldots m_n$.

The manner of dependence of the potentials $\mu_1, \mu_2, \ldots \mu_n$ on the temperature t need concern us very little as we shall always deal with systems maintained at a given constant temperature throughout and shall not need to consider temperature variations. The manner of dependence of the potentials $\mu_1, \mu_2, \ldots \mu_n$ on the pressure p is, on the other hand, of fundamental importance in the treatment of membrane equilibria because in general the pressures of two phases in membrane equilibrium will be unequal. The required relation is obtained by making use of the mathematical identity

$$\frac{\partial}{\partial p}\frac{\partial \zeta}{\partial m_h} = \frac{\partial}{\partial m_h}\frac{\partial \zeta}{\partial p}, \tag{17}$$

where ζ is defined by

$$\zeta = \epsilon - t\eta + pv, \qquad (18)\ [91]$$

and is the characteristic function corresponding to our choice of independent variables $t, p, m_1, m_2, \ldots m_n$. The dependence of variations of ζ on those of the independent variables is given by

$$d\zeta = -\eta dt + vdp + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n. \qquad (19)\ [92]$$

From (19) [92] we see that

$$\frac{\partial \zeta}{\partial m_h} = \mu_h, \qquad (20)$$

and

$$\frac{\partial \zeta}{\partial p} = v. \qquad (21)$$

Substituting from (20) and (21) into (17) we obtain

$$\frac{\partial \mu_h}{\partial p} = \frac{\partial v}{\partial m_h} = v_h, \qquad (22)$$

where v_h denotes the increase in volume of a very large phase when one adds to it unit quantity of the species S_h, keeping the temperature and pressure constant. The volume v_h may be called the "partial volume" of the species S_h.

5. *Mols and Mol Fractions.* Up to this point we have purposely referred to m_h as denoting the number of "units of quantity" of the species S_h without specifying what is this "unit of quantity." Willard Gibbs, living at a time when the molecular theory was less firmly established than at present, chose the same unit of mass for the unit of quantity of each species. In a letter to W. D. Bancroft (Gibbs, I, 434) he agrees, however, that "one might easily economise in letters in the formulae by referring densities (γ) and potentials (μ) to equivalent or molecular weights." We shall therefore adopt this procedure and take as unit quantity of each species the gram-molecule or mol in the highly dilute vapor state. None of the formulae so far given are affected, but the potentials μ now have the dimensions calories per mol instead of calories per gram, and the formulae expressing the dependence of the

potentials μ on the composition take a simpler form. Similarly v_h denotes the increase in volume of a very large phase when one adds to it one mol of the species S_h, keeping temperature and pressure constant. Therefore v_h will be called the "partial molar volume" of the species S_h.

As already mentioned the potentials $\mu_1, \mu_2, \ldots \mu_n$ will be functions not only of t and p but also of the number of mols $m_1, m_2, \ldots m_n$ of the various species in the phase. Actually it is clear that each μ will depend on the composition of the phase but not on the absolute quantity of it. That is to say, $\mu_1, \mu_2, \ldots \mu_n$ will be functions of the quantities $N_1, N_2, \ldots N_n$ defined by

$$\left.\begin{aligned} N_1 &= \frac{m_1}{m_1 + m_2 \ldots + m_n}, \\ N_2 &= \frac{m_2}{m_1 + m_2 \ldots + m_n}, \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ N_n &= \frac{m_n}{m_1 + m_2 \ldots + m_n}. \end{aligned}\right\} \tag{23}$$

The quantities $N_1, N_2, \ldots N_n$ are called the mol fractions of the species $S_1, S_2, \ldots S_n$. They are, of course, not mutually independent but are subject to the identical relation

$$N_1 + N_2 \ldots + N_n = 1, \tag{24}$$

from which it follows that

$$dN_1 + dN_2 \ldots + dN_n = 0. \tag{25}$$

6. Ideal Solutions. A series of solutions in a given solvent are said to be "ideal" if throughout a range of concentrations extending continuously down to pure solvent the potential μ_h of each species S_h whether solvent or solute obeys the formula

$$\mu_h = \mu_h^0(t, p) + At \log N_h, \tag{26}$$

where $\mu_h^0(t, p)$ is independent of the composition of the solution and A is a universal constant known as the "gas constant."

This definition of ideality is exactly equivalent to the condition that for a given temperature and external pressure on a solution the partial vapor pressure of each component shall be directly proportional to its mol fraction.

Since A, t and N_h are all independent of p, it follows from (22) that

$$\frac{\partial \mu_h^0}{\partial p} = v_h. \tag{27}$$

As, by definition, $\mu_h{}^0$ at given temperature and pressure is independent of the composition, it follows that the same is true of v_h. This means that the transference of any part of an ideal solution to another ideal solution in the same solvent takes place, at constant temperature and pressure, without volume contraction or expansion.

For the dependence of v_h on the pressure p we may write

$$v_h = v_h{}^*(1 - \kappa_h p), \tag{28}$$

where $v_h{}^*$ is the value of v_h at vanishing pressure, and where it will always be allowable to assume that κ_h is independent of the pressure p. The compressibility coefficient κ_h may depend on the temperature but this need not concern us.

Owing to the relations (27) and (28) we may replace (26) by

$$\mu_h = \mu_h{}^*(t) + pv_h{}^*(1 - \tfrac{1}{2}\kappa_h p) + At \log N_h, \tag{29}$$

where $\mu_h{}^*(t)$ is independent of the pressure as well as of the composition.

If we now substitute from (29) into the general condition of membrane equilibrium (4) [77], we obtain

$$\begin{aligned} p' v_h{}^*(1 - \tfrac{1}{2}\kappa_h p') + At \log N_h{}' \\ = p'' v_h{}^*(1 - \tfrac{1}{2}\kappa_h p'') + At \log N_h{}'', \end{aligned} \tag{30}$$

or

$$(p' - p'')\, v_h{}^* \left(1 - \kappa_h \frac{p' + p''}{2}\right) = At \log \frac{N_h{}''}{N_h{}'}. \tag{31}$$

Hence

$$p' - p'' = \frac{At}{[v_h]} \log \frac{N_h''}{N_h'}, \tag{32}$$

where $[v_h]$ is defined by

$$[v_h] = v_h^* \left(1 - \kappa_h \frac{p' + p''}{2}\right) \tag{33}$$

and is equal to the partial molar volume of the species S_h at the given temperature and at a pressure equal to the mean of the pressures p' and p'' on either side of the membrane. Formula (32) is exact for membrane equilibrium as regards the species S_h between two ideal solutions in the same solvent, whether S_h denote the solvent species or one of the solute species.

7. *Non-ideal Solutions.* The range of concentrations over which solutions remain ideal varies very much according to the nature of the solvent, the nature of the various solute species and the temperature. It is however generally accepted that in the neighbourhood of infinite dilution all solutions become ideal. This provides a convenient thermodynamic treatment of solutions that are not ideal.

In analogy with (26) we may write formally for any species S_h, whether solvent or solute,

$$\mu_h = \mu_h^0(t, p) + At \log N_h f_h, \tag{34}$$

where $\mu_h^0(t, p)$ is for a given solvent independent of the composition. In general f_h is a function of temperature, pressure and composition, but has the simplifying property that for given temperature and pressure its value approaches unity as the dilution approaches infinity. It is called the activity coefficient of the species S_h and is a measure of the deviation of the solution from ideality so far as the species S_h is concerned.

Since $\mu_h^0(t, p)$ is by definition independent of the composition, and we are assuming that in the neighbourhood of infinite dilution the solutions become ideal, it follows that $\mu_h^0(t, p)$ must be of the same form as for ideal solutions. In accordance with (29) we may therefore write

$$\mu_h = \mu_h^*(t) + pv_h^*(1 - \tfrac{1}{2}\kappa_h p) + At \log N_h f_h, \tag{35}$$

where $\mu_h^*(t)$ is independent of the pressure as well as the composition; v_h^* is the value of the partial molar volume of the species S_h at the given temperature, at zero pressure and at infinite dilution; κ_h is independent of the pressure and the composition; while $v_h^*(1 - \kappa_h p)$ is the value of the partial molar volume of the species S_h at the given temperature, the given pressure and at infinite dilution. The activity coefficient f_h at given temperature and pressure tends to unity at infinite dilution.

If we differentiate (35) with respect to p and use (22) we obtain

$$v_h = \frac{\partial \mu_h}{\partial p} = v_h^* (1 - \kappa_h p) + At \frac{\partial \log f_h}{\partial p} \tag{36}$$

or

$$\frac{\partial \log f_h}{\partial p} = \frac{v_h - v_h^* (1 - \kappa_h p)}{At}. \tag{37}$$

From this we see that the activity coefficient f_h will or will not vary with the pressure at given temperature and composition, according as the partial molar volume v_h in the solution is unequal or equal to its value $v_h^*(1 - \kappa_h p)$ at infinite dilution at the same temperature and pressure.

If we now substitute from (35) into the general condition of membrane equilibrium (4) [77] we obtain

$$\begin{aligned} p' v_h^*(1 - \tfrac{1}{2}\kappa_h p') + At \log N_h' f_h' \\ = p'' v_h^*(1 - \tfrac{1}{2}\kappa_h p'') + At \log N_h'' f_h'' \end{aligned} \tag{38}$$

or

$$(p' - p'')\, v_h^* \left(1 - \kappa_h \frac{p' + p''}{2}\right) = At \log \frac{N_h'' f_h''}{N_h' f_h'}. \tag{39}$$

Hence

$$p' - p'' = \frac{At}{[v_h]} \log \frac{N_h'' f_h''}{N_h' f_h'}, \tag{40}$$

where $[v_h]$ is defined by

$$[v_h] = v_h^* \left(1 - \kappa_h \frac{p' + p''}{2}\right) \tag{41}$$

and is the partial molar volume of the species S_h in an infinitely dilute solution at the given temperature and at a pressure equal to the mean of the pressures p' and p'' on either side of the membrane. Formula (40) is exact for membrane equilibrium as regards the species S_h between two non-ideal solutions of the most general type in the same solvent, whether S_h denote the solvent or one of the solute species. It is important to observe that the values of the activity coefficients to be inserted in the formula are those at the actual pressures at membrane equilibrium, that is f_h' at the pressure p' and f_h'' at the pressure p''.

8. Osmotic Equilibrium. If in particular the membrane is permeable to the solvent only, but impermeable to all the solute species, the membrane equilibrium is called "osmotic equilibrium." If the phase denoted by a double accent is the pure solvent the difference $p' - p''$ is called the "osmotic pressure" of the solution represented by the single accent. In this case, using the suffix 0 to denote the solvent, we have

$$N_0'' = 1, \tag{42}$$

and so the osmotic pressure P in ideal solutions is given by

$$P = p' - p'' = \frac{At}{[v_0]} \log \frac{1}{N_0'}, \tag{43}$$

while in non-ideal solutions it is given by

$$P = p' - p'' = \frac{At}{[v_0]} \log \frac{1}{N_0' f_0'}, \tag{44}$$

the value of f_0' being that at an external pressure p', and $[v_0]$ being the value of the partial molar volume of the pure solvent at the given temperature and at a pressure equal to the mean of those (p' and p'') at either side of the membrane.

9. Incompressible Solutions. If it is allowable to neglect the compressibility κ_0 of the solvent, one need not distinguish between $[v_0]$ and v_0^*, and the formulae for P may be written

$$P = \frac{At}{v_0^*} \log \frac{1}{N_0} \tag{45}$$

for ideal solutions, and

$$P = \frac{At}{v_0^*} \log \frac{1}{N_0 f_0} \tag{46}$$

for non-ideal solutions, the value of f_0 being that corresponding to an external pressure p' somewhat exceeding the osmotic pressure P. From (45) we see that when compressibility is neglected the osmotic pressure of an ideal solution is independent of the external pressure on the pure solvent with which it is in osmotic equilibrium.

10. Relation between Activity Coefficients. The variations of the activity coefficients of the different species with variations of composition at a given temperature and pressure are not completely independent. For according to [98] (Gibbs, I, 88) we have at given temperature and pressure

$$dt = 0, \tag{47.1}$$

$$dp = 0, \tag{47.2}$$

$$m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n = 0, \tag{47.3}$$

or, dividing by $(m_1 + m_2 \ldots + m_n)$,

$$N_1 d\mu_1 + N_2 d\mu_2 \ldots + N_n d\mu_n = 0. \tag{48}$$

If we substitute from (34) or (35) into (48), we obtain

$$N_1 d \log N_1 f_1 + N_2 d \log N_2 f_2 \ldots + N_n d \log N_n f_n = 0. \tag{49}$$

But

$$N_1 d\log N_1 + N_2 d\log N_2 \ldots + N_n d\log N_n$$
$$= dN_1 + dN_2 \ldots + dN_n = 0 \qquad (50)$$

according to (25). It follows from (49) and (50) that

$$N_1 d\log f_1 + N_2 d\log f_2 \ldots + N_n d\log f_n = 0. \qquad (51)$$

From (51) we can conclude in particular that, if throughout a range of concentrations extending down to pure solvent the activity coefficients of all the solute species are unity, then this must also be the case for the solvent species. This is equivalent to the following theorem: If at given temperature and pressure but varying composition every solute species has a partial vapor pressure proportional to its mol fraction (Henry's law), then so has the solvent (Raoult's law).

11. Osmotic Coefficients. Owing to the relation (51), if the mol fraction of the solvent species is almost unity and the mol fractions of all the solute species are very small compared with unity, the value of $\log f_0$ for the solvent species will generally be of a considerably smaller order of magnitude than that of $\log f_s$ for any of the solute species S_s. Thus it is quite usual in a centimolar aqueous solution of a uni-univalent strong electrolyte for the activity coefficient of the solute to be less than unity by about 0.1, while the activity coefficient of the solvent in the same solution will be approximately 1.00006. Thus for purely numerical reasons the activity coefficient of the solvent species, in contrast to the activity coefficient of the solute species, may be an inconvenient function to work with. For this reason it is often convenient to define another function called the "osmotic coefficient" of the solvent, and denoted by g, by the relation

$$1 - g = -\frac{\log f_0}{\log N_0} \qquad (52)$$

or

$$g\log N_0 = \log N_0 f_0. \qquad (53)$$

Using the suffix s to denote solute species and substituting (52) into (51) we obtain

$$N_0\, d\,(\overline{1-g}\cdot\log N_0) = -N_0\, d\log f_0$$

$$= \sum_s N_s\, d\log f_s. \tag{54}$$

If N_0 is almost unity and all the N_s's are very small compared with unity, we have approximately

$$-\log N_0 = -\log\left(1-\sum_s N_s\right) = \sum_s N_s, \tag{55}$$

and (54) becomes approximately

$$d\left(\overline{1-g}\cdot\sum_s N_s\right) + \sum_s N_s\, d\log f_s = 0. \tag{56}$$

From this approximate relation we can conclude that $1-g$ is likely to be of the same order of magnitude as $\log f_s$, or as $1-f_s$. Thus in very dilute solutions not deviating greatly from ideality the osmotic coefficient g will have a more convenient numerical value than the activity coefficient f_0 of the solvent species.

Substituting (53) into (35) we obtain for the chemical potential of the solvent in a non-ideal solution

$$\mu_0 = \mu_0^*(t) + pv_0^*(1-\tfrac{1}{2}\kappa_0 p) + gAt\log N_0. \tag{57}$$

The osmotic coefficient g, like the activity coefficient f_0 of the solvent species, will at given temperature and pressure tend to unity at infinite dilution when the solutions become ideal.

Differentiating (57) with respect to p and using (22) we obtain for the dependence of the osmotic coefficient on the pressure

$$v_0 = v_0^*\,(1-\kappa_0 p) + At\log N_0\cdot\frac{\partial g}{\partial p} \tag{58}$$

or

$$\frac{\partial g}{\partial p} = \frac{v_0 - v_0^*\,(1-\kappa_0 p)}{At\log N_0}. \tag{59}$$

Thus at given temperature and composition the osmotic coefficient, like the activity coefficient of the solvent, will or will not vary with the pressure according as the partial molar volume of the solvent v_0 in the solution is unequal or equal to its value $v_0^*(1 - \kappa_0 p)$ in the pure solvent at the same temperature and pressure.

12. Osmotic Equilibrium in Terms of Osmotic Coefficient. Substituting from (57) into (4) [77] we obtain as the general condition of membrane equilibrium for the solvent between two non-ideal solutions

$$(p' - p'')\, v_0^* \left(1 - \kappa_0 \frac{p' + p''}{2}\right) = At\,(g'' \log N_0'' - g' \log N_0'), \tag{60}$$

or introducing $[v_0]$ the partial molar volume of the pure solvent at the given temperature and at a pressure equal to the mean of those p' and p'' at either side of the membrane,

$$p' - p'' = \frac{At}{[v_0]}\,(g'' \log N_0'' - g' \log N_0'), \tag{61}$$

the values of g' and g'' being those at pressures p' and p'' respectively.

If we assume the membrane to be permeable to the solvent species only, and take the phase denoted by the double accent to be pure solvent, we have

$$\log N'' = 0, \tag{62}$$

and so obtain for the osmotic pressure P

$$P = p' - p'' = g' \frac{At}{[v_0]} \log \frac{1}{N'}, \tag{63}$$

the value of g' being that at an external pressure p'.

If it is allowable to neglect the compressibility of the solvent one need not distinguish between $[v_0]$ and v_0^*, in which case instead of (63) one may write

$$P = g' \frac{At}{v_0^*} \log \frac{1}{N'}, \tag{64}$$

the value of g' being that at an external pressure p' somewhat greater than P.

Comparing (64) with (45) we see that, when we neglect the compressibility, the osmotic coefficient is the ratio of the actual osmotic pressure in a non-ideal solution to its value in an ideal solution of the same composition. This is the origin of the name "osmotic coefficient."

13. Extremely Dilute Solutions. If a solution, whether ideal or non-ideal, is so dilute that the mol fractions N_s of all the solute species are extremely small compared with that of the solvent N_0, we may make the three approximations:

$$\log \frac{1}{N_0} = -\log\Big(1 - \sum_s N_s\Big) = \sum_s N_s, \tag{65}$$

$$N_s = \frac{m_s}{m_0 + \sum_s m_s} = \frac{m_s}{m_0}, \tag{66}$$

$$v = m_0 v_0 + \sum_s m_s v_s = m_0 v_0{}^*. \tag{67}$$

Formula (45) for ideal solutions then takes the approximate form

$$P = \frac{At}{v} \sum_s m_s = At \sum_s \gamma_s, \tag{68}$$

where γ_s denotes volume concentration. Similarly formula (46) for non-ideal solutions takes the approximate form

$$P = g\, At \sum_s \gamma_s. \tag{69}$$

Formula (68) is contained in some fragmentary material by Willard Gibbs published after his death (Gibbs, I, 421, equation [7]). For its approximate validity it is necessary to assume not merely that the solution is ideal and incompressible, but also that it is extremely dilute. This formula was originally due to van't Hoff, who realised its limitations. It has unfortunately been applied only too often under conditions where it cannot be even approximately correct.

14. Electric Potential Difference between Two Identical Phases. Up to this point we have tacitly assumed that all the species present were electrically neutral. The fundamental difference between the behavior of ions and of uncharged species is the following. The potential of an uncharged species in a phase at given temperature and pressure is completely determined by the bulk composition of the phase, and is independent of the presence of any impurity at the surface as long as its concentration in the bulk is negligible. This, however, is not the case for ions. Let us consider two phases identical with respect to temperature, pressure, size, shape and bulk composition. Then it may be that the first phase contains an excess of ions of one or more kinds over the second phase, this excess being so small that its effect on the size, shape and bulk concentration of the phase is entirely negligible. If however the total excess of ions in the first phase over those in the second has a net electric charge, the corresponding excess charge will be distributed over the surface of the first phase, and the potential of any ionic species within the phase will be affected thereby. The difference between the potential of a given ionic species in the first phase and in the second will be determined entirely by the difference in distribution of electric charge over the surfaces of the two phases and independent of the chemical nature of the excess ions. One might describe the situation roughly by saying that the excess ions in the first phase over those in the second are too few to show themselves in any manner except by their electrical effect. It is usual and convenient to refer to two such phases as "of identical composition but at different electric potentials." To emphasize the peculiar property of the potential of an ionic species, that it is not completely determined by the bulk composition of the phase, a slightly modified symbol will be used. The potential of the ionic species S_i will be denoted by $[\mu_i]$. The difference between its value in the two phases of identical composition will be of the form

$$[\mu_i]' - [\mu_i]'' = z_i F(V' - V'') \tag{70}$$

where z_i denotes the valency (positive or negative) of the ionic species S_i and F denotes the faraday, so that z_iF is the charge of one mol of the ionic species. Finally V', V'' have values independent of the type of ion being considered, and $V' - V''$ is called the "electric potential difference" between the two phases.

This may at first sight appear a strange method of defining electric potential difference between two phases of "identical" composition, but it does not seem possible to give a simpler definition that is not ambiguous. The usual definition of the mathematical theory of electrostatics is not applicable to thermodynamic systems, for the conditions of thermodynamic equilibrium of ions are by no means the same as the conditions of equilibrium of "static electricity."

15. Electric Potential Difference between Two Phases of Different Composition. If we now consider the difference of the potential of a given ionic species between two phases of different bulk composition, this difference will be determined partly by the difference in the chemical composition in the bulk and partly by the distribution of electric charge at the surfaces. This may be expressed formally as

$$[\mu_i]' - [\mu_i]'' = (\mu_i' - \mu_i'') + z_iF(V' - V''), \qquad (71)$$

where $[\mu_i]$ denotes the potential of the ionic species, μ_i denotes the part of the potential due to the chemical composition of the phase and z_iFV the part due to the distribution of electric charge at its surface. The quantity $[\mu_i]$ may be called the "electrochemical potential" of the species S_i, μ_i may be called the "chemical potential" of the species S_i, and V may be called the "electric potential."

When, however, we come to ask ourselves exactly what would be meant by the statement that the electric potential V had the same value in two phases of different composition, we would have to admit that the statement had in general no physical significance. All equilibria and changes towards equilibrium are completely determined by the electrochemical potentials $[\mu_i]$, and any decomposition of $[\mu_i]$ into two terms μ_i and z_iFV is in general arbitrary. This attitude is in accordance with a remark of Willard Gibbs (Collected Works, I, 429): "Again, the consideration of the difference of potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involves the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in 'pieces of metal of the same kind attached to the electrodes' is exactly one of the things which we can and do measure." Unfortunately not all chemists have been as careful as Willard Gibbs in avoiding the expression "difference of electric potential" when referring to two phases of different composition.

16. Combinations of Ions with Zero Net Electric Charge. The potential $[\mu_i]$ of a given ionic species in a certain phase is the increase in the characteristic function when one mol of the given species is added to the phase, keeping all the other independent variables unaltered. In particular it is the increase in ζ when one mol is added at constant temperature and pressure. If we consider, not the addition of a single ionic species but the simultaneous addition or removal of several species, say the addition of λ_i mols of the species S_i, where λ_i may be positive or negative, then the corresponding increase in ζ will be $\sum_i \lambda_i [\mu_i]$.

Making the substitution in (71) we have formally

$$\sum_i \lambda_i [\mu_i] = \sum_i \lambda_i \mu_i + FV \sum_i \lambda_i z_i. \tag{72}$$

Suppose now that the net electric charge of the ions added is zero. The condition for this is

$$\sum_i \lambda_i z_i = 0. \tag{73}$$

If this condition is satisfied then (72) becomes

$$\sum_i \lambda_i [\mu_i] = \sum_i \lambda_i \mu_i. \tag{74}$$

Thus, although the chemical potential of an individual ionic species is indeterminate, certain linear combinations of the chemical potentials of ionic species are determinate and, in fact, equal to the corresponding linear combinations of the electrochemical potentials, the condition for this being that the linear combination corresponds to a combination of ions with zero net electric charge. The physical meaning of this is simply that the potential of a combination of ions with zero net electric charge is determined completely by the chemical composition in the bulk of the phase and is independent of its electrical state.

17. Ideal Solutions of Ions. At very high dilutions of ions all equilibria are given correctly by assuming that the electrochemical potential $[\mu_i]$ of the ionic species S_i is of the form

$$[\mu_i] = \mu_i^*(t) + pv_i^*(1 - \tfrac{1}{2}\kappa_i p) + At \log N_i + z_i FV, \tag{75}$$

where $\mu_i^*(t)$ is for a given solvent a function of the temperature only, v_i^* and $v_i^*(1 - \kappa_i p)$ are the partial molar volumes of the ionic species S_i at zero pressure and at the pressure p respectively, N_i is the mol fraction of the species S_i, and z_i its valency. Finally V depends on the "electrical state" of the system, that is, on the distribution of electric charges at the surface of the phase, and has the same value for all ionic species. Solutions of ions behaving in accordance with (75) are called "ideal." In analogy with ideal solutions of uncharged species it is natural to define the chemical potential μ_i of the ionic species S_i by

$$\mu_i = \mu_i^*(t) + pv_i^*(1 - \tfrac{1}{2}\kappa_i p) + At \log N_i, \tag{76}$$

and to call V the electric potential of the phase.

18. Non-ideal Solutions of Ions. Since all ionic solutions tend towards ideality at infinite dilution, it is most convenient to treat non-ideal solutions by the introduction of activity coefficients f_i just as in the case of non-ideal solutions of uncharged species. We therefore write formally

$$[\mu_i] = \mu_i^*(t) + pv_i^*(1 - \tfrac{1}{2}\kappa_i p) + At \log N_i \\ + At \log f_i + z_i FV, \tag{77}$$

where $\mu_i^*(t)$ is for a given solvent a function of the temperature only; v_i^* and $v_i^*(1 - \kappa_i p)$ are the values of the partial molar volume of the species S_i at infinite dilution at the given temperature, and at zero pressure and at the given pressure p respectively; N_i is the mol fraction of the species S_i; z_i its valency; and f_i its activity coefficient which, at given temperature and pressure, tends to unity at infinite dilution. Finally, V has the same value for all ionic species in the given phase.

Formula (77) will always lead to correct physical results, but it is partly ambiguous because there is no experimental method of distinguishing between the last two terms,

$$At \log f_i + z_i FV. \tag{78}$$

Thus the activity coefficient of a single ionic species is physically indeterminate, as in each phase an arbitrary value may be assigned to V and the value of f_i will vary in such a way that the sum (78) remains invariant. If, however, we consider combinations of ions with zero net electric charge, the corresponding combinations of electrochemical potentials will be given by

$$\sum_i \lambda_i [\mu_i] = \sum_i \lambda_i \mu_i^* [t] + p_i \sum_i \lambda_i v_i^* (1 - \tfrac{1}{2} \kappa_i p)$$
$$+ At \sum_i \lambda_i \log N_i + At \sum_i \lambda_i \log f_i, \tag{79}$$

since by supposition the λ_i's satisfy the relation (73). It follows that, although the individual ionic activity coefficients f_i are physically indefinite, certain combinations of them of the form

$$\sum_i \lambda_i \log f_i, \tag{80}$$

or

$$\prod_i (f_i)^{\lambda_i}, \tag{81}$$

are completely determinate whenever the λ_i's satisfy (73).

19. Mean Activity Coefficient of Electrolyte. Of the various possible products of activity coefficients of the type (81) which are physically determinate, the most important is the "mean activity coefficient" of an electrolyte. Thus for an electrolyte consisting of q_+ positive ions of valency z_+ and q_- negative ions of valency z_-, the condition of electrical neutrality is

$$q_+z_+ + q_-z_- = 0. \tag{82}$$

It follows that the quantity $f_\pm$, defined by

$$q_+ \log f_+ + q_- \log f_- = (q_+ + q_-) \log f_\pm, \tag{83}$$

where f_+, f_- are the ionic activity coefficients, or by

$$(f_\pm)^{q_+ + q_-} = (f_+)^{q_+}(f_-)^{q_-}, \tag{84}$$

is completely determinate although the ionic activity coefficients f_+ and f_- are to some extent arbitrary. The function $f_\pm$ is called the mean activity coefficient of the electrolyte.

Another example of a combination of ionic activity coefficients that is definite is the ratio of the activity coefficients of two cations, or of two anions, in the same solution and of the same valency.

20. Membrane Equilibrium of Ideal Ionic Solutions. We are now in a position to write down directly the conditions of membrane equilibrium for ionic solutions. We have merely to substitute the values of the potentials $[\mu_i]$ in the general condition of membrane equilibrium

$$[\mu_i]' = [\mu_i]''. \tag{85}$$

For ideal solutions we obtain according to (75)

$$\begin{aligned} p' v_i^*(1 - \tfrac{1}{2}\kappa_i p') &+ At \log N_i' + z_i FV' \\ &= p'' v_i^*(1 - \tfrac{1}{2}\kappa_i p'') + At \log N_i'' + z_i FV''. \end{aligned} \tag{86}$$

Introducing $[v_i]$, the partial molar volume at infinite dilution at the given temperature and at a pressure equal to the mean of those (p' and p'') at either side of the membrane, this becomes

$$At \log \frac{N_i''}{N_i'} = (p' - p'')[v_i] + z_i F(V' - V''). \tag{87}$$

Comparing formula (87) for two ionic species i and h of the same valency z, we obtain

$$At \log \frac{N_i''}{N_h''} \frac{N_h'}{N_i'} = (p' - p'')([v_i] - [v_h]). \tag{88}$$

The right hand side of (88) will generally be small compared with At and may often with sufficient accuracy be regarded as zero. With this approximation (88) simplifies to

$$\frac{N_i'}{N_h'} = \frac{N_i''}{N_h''}. \tag{89}$$

Applying formula (87) to the two ionic species of an electrolyte composed of q_+ cations of valency z_+ and q_- anions of valency z_-, we obtain

$$At \log \left(\frac{N_+''}{N_+'}\right)^{q_+} \left(\frac{N_-''}{N_-'}\right)^{q_-} = (p' - p'')(q_+[v_+] - q_-[v_-]). \tag{90}$$

The right hand side of (90) will generally be small compared with At and may often with sufficient accuracy be regarded as zero. To this degree of accuracy we may replace the exact formula (90) by the approximate one

$$(N_+')^{q_+} (N_-')^{q_-} = (N_+'')^{q_+}(N_-'')^{q_-}. \tag{91}$$

If we compare (90) for the membrane equilibrium of a solute electrolyte with (32) for the equilibrium of the uncharged solvent, we obtain

$$\log \left(\frac{N_+''}{N_+'}\right)^{q_+} \left(\frac{N_-''}{N_-'}\right)^{q_-} = \frac{q_+[v_+] + q_-[v_-]}{[v_0]} \log \frac{N_0''}{N_0'} \tag{92}$$

or

$$\frac{(N_+')^{q_+} (N_-')^{q_-}}{(N_0')^r} = \frac{(N_+'')^{q_+} (N_-'')^{q_-}}{(N_0'')^r}, \tag{93}$$

where r is defined by

$$r = \frac{q_+[v_+] + q_-[v_-]}{[v_0]} \tag{94}$$

and is the ratio of the partial molar volume of the electrolyte to that of the solvent, both at the given temperature and at a pressure equal to the mean of those at either side of the membrane. At extreme dilutions the mol fraction N_0 of the solvent differs very slightly from unity, and (93) approximates to (91).

21. Membrane Equilibrium of Non-ideal Ionic Solutions. The corresponding formulae for non-ideal solutions are obtained similarly by substituting from (77) in the general condition of membrane equilibrium,

$$[\mu_i]' = [\mu_i]''. \tag{95}$$

For two ionic species i and h of the same valency, we obtain in analogy with (88)

$$At \log \frac{N_i'' f_i''}{N_h'' f_h''} \frac{N_h' f_h'}{N_i' f_i'} = (p' - p'')([v_i] - [v_h]), \tag{96}$$

where $[v_i]$, $[v_h]$ are the values of the partial molar volumes at infinite dilution at the given temperature and at a pressure equal to the mean of those (p' and p'') at either side of the membrane. It is to be observed that the combinations of activity coefficients occurring in (96) are the ratios of the activity coefficients for two ions of the same valency and are therefore physically definite. If the right hand side of (96) is negligibly small compared to At, then (96) approximates to the simple relation

$$\frac{N_i' f_i'}{N_h' f_h'} = \frac{N_i'' f_i''}{N_h'' f_h''}. \tag{97}$$

For the membrane equilibrium of an electrolyte consisting of q_+ cations of valency z_+ and q_- anions of valency z_-, the exact formula obtained from (77) and (95) is, in analogy with (90),

$$At \log \left(\frac{N_+''}{N_+'}\right)^{q_+} \left(\frac{N_-''}{N_-'}\right)^{q_-} \left(\frac{f_\pm''}{f_\pm'}\right)^{q_+ + q_-}$$
$$= (p' - p'')(q_+[v_+] + q_-[v_-]), \tag{98}$$

which involves only the mean activity coefficients $f_\pm$ of the electrolyte in the two phases. If the right hand side of (98) is negligibly small compared with At, then the exact formula (98) may be replaced by the approximate one

$$(N_+')^{q_+}(N_-')^{q_-}(f_\pm')^{q_++q_-} = (N_+'')^{q_+}(N_-'')^{q_-}(f_\pm'')^{q_++q_-}. \quad (99)$$

The corresponding formula for the membrane equilibrium of a single ionic species in non-ideal solutions takes the form

$$At \log \frac{N_i''}{N_i'} + At \log \frac{f_i''}{f_i'} = (p' - p'')\,[v_i] + z_i\,F(V' - V'') \quad (100)$$

but tells us nothing, as neither the term $At \log \frac{f_i''}{f_i'}$ on the left nor the term $z_i\,F(V' - V'')$ on the right is physically determinable.

22. Contact Equilibrium. A most important case of membrane equilibrium is that of two phases with one common component ion, the surface of separation forming a natural membrane permeable to the common ion but impermeable to all others. This may be referred to as "contact equilibrium." For example, for two metals in contact, say Cu and Zn, there is equilibrium between the two phases as regards electrons El^- but not as regards the positive ions Cu^{++} or Zn^{++}. The equilibrium is completely defined by

$$[\mu_{El^-}]^{Cu} = [\mu_{El^-}]^{Zn}, \quad (101)$$

the suffix denoting, as usual, the component, and the index the phase. Similarly for a metallic electrode of Cu, dipping into a solution S containing ions of this metal, in this case Cu^{++}, the contact equilibrium is completely defined by

$$[\mu_{Cu^{++}}]^{Cu} = [\mu_{Cu^{++}}]^{S}, \quad (102)$$

the electrode and solution being in equilibrium as regards the metallic ions only. In neither of these cases of contact equilibrium is any "contact electric potential difference" thermodynamically definable.

23. Purely Chemical Cell. Consider the system composed of the following phases and membranes arranged in order, each phase being separated by partially permeable membranes from its neighbouring phases, and completely separated from the remaining phases.

Phase α. Containing, *inter alia*, species A and B.
Membrane 1. Permeable to B only.
Phase β. Containing, *inter alia*, species B and C.
Membrane 2. Permeable to C only.
Phase γ. Containing, *inter alia*, species C and A.

If all the species A, B, C are electrically neutral, the two membrane equilibria are determined completely by the conditions

$$\mu_B^\beta = \mu_B^\alpha, \tag{103.1}$$

$$\mu_C^\gamma = \mu_C^\beta, \tag{103.2}$$

but in general

$$\mu_A^\gamma \neq \mu_A^\alpha, \tag{103.3}$$

that is, the phases γ and α are not in equilibrium as regards the species A. If the phases γ and α be now brought into contact through a membrane permeable to A only, there will be a flow of A from the one to the other in a direction determined by the sign of $\mu_A^\gamma - \mu_A^\alpha$. This flow will, of course, upset the other membrane equilibria, which will readjust themselves. The flow of A through the auxiliary membrane and the accompanying readjustments will not cease until either the phases γ and α are again separated, or the conditions

$$\mu_B^\beta = \mu_B^\alpha, \tag{104.1}$$

$$\mu_C^\gamma = \mu_C^\beta, \tag{104.2}$$

$$\mu_A^\gamma = \mu_A^\alpha, \tag{104.3}$$

are satisfied simultaneously.

We may call the system just described a "purely chemical cell," and the difference

$$\mu_A^\gamma - \mu_A^\alpha \tag{105}$$

the "chemico-motive force" of the cell for the component A. Bringing the phases γ and α into contact through a membrane permeable only to A we may call short-circuiting the cell, and separating these phases "breaking the circuit." When the conditions (104) are satisfied simultaneously we may say that the cell is "run down."

More complicated "purely chemical cells" might be described, containing a larger number of phases, membranes and components, but the general nature of any such cell and the conditions of equilibrium will be similar to that of the above simple example.

The "purely chemical cell" is not of practical importance and, possibly for this reason, is not usually described or discussed in text-books. It has been described here since a clear understanding of a "purely chemical cell" should facilitate a complete comprehension of the nature of an "electrochemical cell," which will be discussed next. It is especially to be emphasized that from a theoretical thermodynamic point of view the electric charges of the ions are rather incidental, the fundamental factors at the base of any cell, whether "purely chemical" or "electrochemical," being the membrane or contact equilibria between successive phases.

24. Electrochemical Cells. The only essential difference between an "electrochemical cell" and a "purely chemical cell" is that in the former the membrane equilibria involve charged ions. Let us consider the following system, somewhat similar to the purely chemical cell discussed above, in which however the various species concerned are ions.

Phase α. Containing ions E and A.
Membrane 1. Permeable to ions A only.
Phase β. Containing ions A and B.
Membrane 2. Permeable to ions B only.
Phase γ. Containing ions B and E.
Membrane 3. Permeable to ions E only.
Phase α'. Chemically identical with phase α.

The three membrane equilibria are defined completely by the conditions:

$$[\mu_A]^\beta = [\mu_A]^\alpha, \tag{106.1}$$

$$[\mu_B]^\gamma = [\mu_B]^\beta, \tag{106.2}$$

$$[\mu_E]^{\alpha'} = [\mu_E]^\gamma, \tag{106.3}$$

but in general

$$[\mu_E]^{\alpha'} \neq [\mu_E]^{\alpha}. \tag{106.4}$$

As compared with the example of a purely chemical cell, we have included in the present system one extra phase and membrane in order that the two extreme phases or "terminals" α and α' should have the same chemical composition. We may therefore write

$$[\mu_E]^{\alpha'} - [\mu_E]^{\alpha} = z_E F(V^{\alpha'} - V^{\alpha}), \tag{107}$$

and the difference of electric potential $(V^{\alpha'} - V^{\alpha})$ thus defined is called the "electromotive force" E of the cell. Putting the two phases α' and α into contact is called short-circuiting the cell and separating them "breaking the circuit." On closing the circuit there will be an adjustment of membrane equilibria with net flow of electric charge round the circuit in a direction determined by the sign of E. This will cease when the conditions

$$[\mu_A]^{\beta} = [\mu_A]^{\alpha}, \tag{108.1}$$

$$[\mu_B]^{\gamma} = [\mu_B]^{\beta}, \tag{108.2}$$

$$[\mu_E]^{\alpha'} = [\mu_E]^{\gamma} = [\mu_E]^{\alpha}, \tag{108.3}$$

are satisfied simultaneously, when the cell is said to be "run down."

We will now give a concrete example. We suppose the ionic species A to be Cu^{++}, B to be Zn^{++}, and E to be electrons El^- and thus obtain the cell

$$\begin{array}{c|c|c|l} Cu & \text{Solution } S \text{ containing } Cu^{++} \text{ and } Zn^{++} & Zn & Cu. \\ \alpha & & & \alpha' \end{array}$$

We also imagine the boundaries between the phases to form natural membranes, each permeable to only one ionic species. In practice there would be irreversible deposition of copper on the zinc, and this cell would not function unless some means of preventing Cu^{++} ions from coming into contact with the metal Zn were provided. We have oversimplified the description of the cell in order to avoid a discussion of diffusion potentials. A workable cell would be the following:

$$\begin{array}{l|l|l|c|l} Cu & \text{Solution } S_1 \text{ containing} & \text{Solution } S_2 \text{ containing} & & \\ & \quad Cu^{++} \text{ and large excess} & \quad Zn^{++} \text{ and large excess} & Zn & Cu. \\ & \quad \text{of other ions} & \quad \text{of other ions} & & \end{array}$$

The diffusion potential between the two solutions S_1 and S_2 could be made negligible by making the composition of the two solutions substantially the same apart from the Cu^{++} ions in the one and Zn^{++} ions in the other, the concentration of these being in both cases small compared with the concentrations of the other cations.

In the metallic phases we have the purely chemical, homogeneous equilibrium conditions

$$[\mu_{Cu^{++}}]^{Cu} + 2\,[\mu_{El\text{-}}]^{Cu} = \mu_{Cu}^{Cu}, \tag{109.1}$$

$$[\mu_{Zn^{++}}]^{Zn} + 2\,[\mu_{El\text{-}}]^{Zn} = \mu_{Zn}^{Zn}, \tag{109.2}$$

where μ_{Cu}^{Cu} and μ_{Zn}^{Zn} are independent of the electric states of the respective phases. The contact equilibrium conditions are

$$[\mu_{Cu^{++}}]^{S} = [\mu_{Cu^{++}}]^{\alpha}, \tag{110.1}$$

$$[\mu_{Zn^{++}}]^{Zn} = [\mu_{Zn^{++}}]^{S}, \tag{110.2}$$

$$[\mu_{El\text{-}}]^{\alpha'} = [\mu_{El\text{-}}]^{Zn}. \tag{110.3}$$

Combining (107), (109), (110) we obtain for the electromotive force E

$$\begin{aligned} 2\,FE &= [\mu_{Cu^{++}}]^{\alpha'} - [\mu_{Cu^{++}}]^{\alpha} \\ &= \mu_{Cu}^{Cu} - \mu_{Zn}^{Zn} + [\mu_{Zn^{++}}]^{S} - [\mu_{Cu^{++}}]^{S}, \end{aligned} \tag{111}$$

or, in terms of activity coefficients,

$$E = E^0 + \frac{At}{2\,F} \log \frac{N_{Zn^{++}}^{S}}{N_{Cu^{++}}^{S}} \cdot \frac{f_{Zn^{++}}^{S}}{f_{Cu^{++}}^{S}}, \tag{112}$$

where E^0 is independent of the composition of the solution, the values of the mol fractions N^S and activity coefficients f^S being those in the solution.

More detailed discussion of electrochemical cells would be outside our province, but the above example serves to show that the electromotive force of any cell may be computed by regarding the mechanism of the cell as a combination of several membrane equilibria. The electromotive force E is equal to the difference of potential of any univalent positive ion in the two terminals of the same metal at the two ends of the cell. This is the only electric potential difference that is measured, and is the only one to which any reference is made in this treatment. As already mentioned, this attitude towards the conception of electric potential is in accordance with views expressed by Willard Gibbs.

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F

THE QUANTITIES χ, ψ, ζ, AND THE CRITERIA OF EQUILIBRIUM

[*Gibbs, I, pp. 89–92*]

E. A. MILNE

THE following notes amount to an independent treatment of Gibbs' results in this section. They also include an extension of some of his calculations so as to take account of second order terms where discussion of first order terms alone ("differentials") is insufficient. Some of the later calculations are adapted from Lewis and Randall's *Thermodynamics*.

1. Stability Tests. At the beginning of his memoir, *The Equilibrium of Heterogeneous Substances*, Gibbs establishes criteria of stability which may be stated as follows: Let Δ denote any increment of a quantity, not necessarily small. Let d denote a "differential" of the quantity, which may (non-rigorously) be identified approximately with a *small* increment.

Then if ϵ denotes the energy of a system, η its entropy, we have:

For stable equilibrium,

$$(\Delta\eta)_\epsilon < 0 \text{ or } (\Delta\epsilon)_\eta > 0.$$

For neutral equilibrium, in general,

$$(\Delta\eta)_\epsilon \leqq 0 \text{ or } (\Delta\epsilon)_\eta \geqq 0,$$

but there exist variations for which

$$(\Delta\eta)_\epsilon = 0 \text{ or } (\Delta\epsilon)_\eta = 0.$$

For unstable equilibrium,

$$(d\eta)_\epsilon = 0 \text{ or } (d\epsilon)_\eta = 0,$$

but there exist variations for which

$$(\Delta\eta)_\epsilon > 0 \text{ or } (\Delta\epsilon)_\eta < 0.$$

In the above, the subscript denotes that the corresponding variable is maintained constant in the variation.

Gibbs proceeds, in the section under consideration (Gibbs, I, 89–92), to establish the equivalence of the above to similar variational conditions involving
(1) the *work function* ψ, defined by $\psi = \epsilon - t\eta$,
(2) the *heat function* χ, defined by $\chi = \epsilon + pv$,
(3) the *free energy function* ζ, defined by $\zeta = \epsilon - t\eta + pv$.
He gives a method of proof which is sound in principle, and which suggests the method to adopt, but which does not distinguish between small variations and finite variations. The following includes the substance of Gibbs' results, and supplies proofs in certain cases where Gibbs left the proof to the reader.

2. The Work Function. The value of the criteria about to be discussed is that they render the general criteria more easily applicable to certain particular cases, by restricting the type of variation permitted. For example, in certain cases they impose a condition of constancy of volume in addition to constancy of entropy, in discussing changes of energy.

We shall now prove that the condition

$$(\Delta\psi)_{t,v} \geqq 0 \tag{1}$$

is equivalent to the condition

$$(\Delta\epsilon)_{\eta,v} \geqq 0. \tag{2}$$

For suppose that there exists a neighbouring state for which

$$(\Delta\epsilon)_{\eta,v} < 0.$$

We shall prove that there then exists a state for which

$$(\Delta\psi)_{t,v} < 0.$$

This will ensure that if we are given that (1) is true, no contradiction of (2) can exist; hence (1) implies (2).

For, if the neighbouring state for which $(\Delta\epsilon)_{\eta,v} < 0$ is not one of uniform temperature, let its temperatures be equalized at constant volume. This can only increase its entropy. Now remove heat so as to reduce the entropy to the initial value, at the same volume. This process reduces the energy. Thus we have constructed a state of *uniform temperature* for which

$$(\Delta\epsilon)_{\eta,\,v} < 0.$$

Now we have $\psi = \epsilon - t\eta$, whence in general

$$\Delta\psi = \Delta\epsilon - t\Delta\eta - \eta\Delta t - \Delta t\Delta\eta.$$

In our case

$$\Delta\eta = 0, \text{ and so } \Delta\psi = \Delta\epsilon - \eta\Delta t$$

or

$$\Delta\psi + \eta\Delta t = \Delta\epsilon < 0, \tag{3}$$

by hypothesis.

Now add or subtract heat at constant volume. For such a process the infinitesimal increment in energy, say $d'\epsilon$ is given by

$$d'\epsilon = t\,d'\eta,$$

whilst similarly

$$d'\psi = d'\epsilon - \eta\,d't - t\,d'\eta,$$

i.e.,

$$d'\psi = -\eta\,d't.$$

It follows that the *finite* increment in ψ, namely $\Delta'\psi$, is given by

$$\Delta'\psi = -\int_t^{t+\Delta' t} \eta\,d't. \tag{4}$$

Accordingly, by (3) and (4),

$$\Delta\psi + \Delta'\psi < -\eta\Delta t + \int_{t+\Delta' t}^{t} \eta\,d't.$$

Now choose $\Delta' t = -\Delta t$, thus restoring the initial temperature (a state for which ψ is defined is of course necessarily a state of *uniform* temperature). We have then

$$\Delta\psi + \Delta'\psi < -\eta\Delta t + \int_{t_0 - \Delta t}^{t_0} \eta\, d't,$$

where now t_0 denotes the initial temperature. This gives

$$\Delta\psi + \Delta'\psi < -\eta_0\,\Delta t + \int_{t_0 - \Delta t}^{t_0} \left[\eta_0 + \left(\frac{\partial\eta}{\partial t}\right)_0 (t - t_0) + \ldots\right] d't,$$

where η_0 denotes the initial entropy. Evaluating the integral we have

$$\Delta\psi + \Delta'\psi < -\tfrac{1}{2}\left(\frac{\partial\eta}{\partial t}\right)_0 (\Delta t)^2 + \ldots$$

Now $\left(\frac{\partial\eta}{\partial t}\right)_0$ is positive. Hence, provided Δt is sufficiently small,

$$\Delta\psi + \Delta'\psi < 0.$$

We have thus constructed a state for which the total (finite) increment in ψ, namely $(\Delta + \Delta')\psi$, is negative, contradicting (1). Moreover it is a state of the same (initial) temperature and volume. This demonstrates that (1) implies (2). The proof of the converse may be left to the reader. The above establishes for a finite change Gibbs' result [111], established by him by less rigorous methods in equations [112] and [115] (Gibbs, I, 91).

3. The Free Energy Function. In equation [117] Gibbs states without proof that the condition of equilibrium may be written

$$(\delta\zeta)_{t,\,p} \geqq 0.$$

We shall prove that

$$(\Delta\psi)_{t,\,v} \geqq 0 \tag{5}$$

and

$$(\Delta\zeta)_{t,\,p} \geqq 0 \tag{6}$$

are equivalent.

We will first show that (5) implies (6). To do this we will show that if there exists a state violating (6) then there exists a state violating (5). If then (5) is known to hold, there can be no state violating (6), and so (6) holds.

Let us then suppose that a state exists for which

$$(\Delta\zeta)_{t,\,p} < 0.$$

Now

$$\zeta = \psi + pv,$$

and so

$$\Delta\zeta = \Delta\psi + p\Delta v + v\Delta p + \Delta v\Delta p.$$

Here $\Delta p = 0$, and hence

$$\Delta\zeta = \Delta\psi + p\Delta v < 0.$$

Therefore

$$\Delta\psi < -p\Delta v. \tag{7}$$

Now change the volume and pressure reversibly at constant temperature. For these changes the *infinitesimal* increments are given by

$$d'\epsilon = t\,d'\eta - p\,d'v$$

by the first and second laws of thermodynamics. Hence

$$d'\psi = d'(\epsilon - t\eta) = -p\,d'v,$$

since $d't = 0$. It follows that

$$\Delta'\psi = -\int_{v_0}^{v_0+\Delta' v} p\,d'v,$$

whence

$$\Delta\psi + \Delta'\psi < -p\Delta v + \int_{v_0+\Delta' v}^{v_0} p\,d'v.$$

Now choose $\Delta' v = -\Delta v$, thus restoring the initial volume. Then

$$(\Delta\psi + \Delta'\psi)_{t,v} < -p\Delta v + \int_{v_0 - \Delta v}^{v_0} p\, d'v$$

$$< -p_0\Delta v + \int_{v_0 - \Delta v}^{v_0} \left[p_0 + \left(\frac{\partial p}{\partial v}\right)_0 (v - v_0) + \ldots \right] d'v$$

$$< -\left(\frac{\partial p}{\partial v}\right)_0 \cdot \tfrac{1}{2}(\Delta v)^2,$$

where p_0 denotes the initial pressure.

At this point we encounter a difficulty. For $\left(\frac{\partial p}{\partial v}\right)_0$ is negative, and so we have apparently only established that the total increment in ψ, namely $(\Delta + \Delta')\psi$, is less than a positive quantity. We have thus apparently not proved that it is negative. But if we examine the argument, we see that the original increment in ζ, namely $\Delta\zeta$, must be in general of the order Δv, and in fact there exists a constant c such that $\Delta\zeta < c|\Delta v|$, where $c < 0$. This means that (7) may be replaced by

$$\Delta\psi < -p\Delta v + c\,|\,\Delta v\,|,$$

whence

$$(\Delta + \Delta')\,\psi < c|\Delta v| - \left(\frac{\partial p}{\partial v}\right)_0 \cdot \tfrac{1}{2}\,(\Delta v)^2.$$

Hence *in general*

$$[(\Delta + \Delta')\psi]_{t,v} < 0,$$

which contradicts (5) and so establishes our result. The difficulty here encountered demonstrates the great need for care in establishing thermodynamic inequalities. The reader may find it necessary to overcome a similar difficulty in the proof left to him in the preceding section.

It is less difficult to prove the converse. Suppose now that we are given a state for which

$$(\Delta\psi)_{t,v} < 0.$$

If this state is not one of uniform pressure, let the pressure equalize itself at constant temperature and constant volume. Then by general theory, since this is an irreversible process, the function ψ must decrease in the process. (For if Δ'' denotes the change in question, and $\Delta''Q$ is the heat absorbed

$$\Delta''\eta \geqq \Delta''Q/t = \Delta''\epsilon/t,$$

or

$$\Delta''\epsilon - t\,\Delta''\eta \leqq 0, \text{ or } \Delta''\psi < 0.)$$

Hence we have constructed a new state of *uniform* pressure for which

$$(\Delta\psi)_{t,\,v} < 0.$$

Now

$$\Delta\zeta = \Delta(\psi + pv)$$

and here $\Delta v = 0$. Hence

$$\Delta\zeta = \Delta\psi + v\Delta p,$$

or

$$\Delta\zeta < v\Delta p.$$

Now change the pressure and volume reversibly at constant temperature. For this change, *infinitesimal* increments are given by

$$d'\epsilon = t\,d'\eta - p\,d'v,$$

$$d'\zeta = d'(\epsilon - \eta t + pv)$$

$$= v\,d'p,$$

since $d't = 0$. Hence the new *finite* increment $\Delta'\zeta$ is given by

$$\Delta'\zeta = \int_{p_0}^{p_0 + \Delta'p} v\,d'p,$$

and accordingly

$$\Delta\zeta + \Delta'\zeta < v\Delta p + \int_{p_0}^{p_0 + \Delta' p} v\, d'p.$$

Now choose $\Delta' p = -\Delta p$, thus restoring the initial pressure. Then

$$\Delta\zeta + \Delta'\zeta < v_0 \Delta p - \int_{p_0 - \Delta p}^{p_0} \left[v_0 + \left(\frac{\partial v}{\partial p}\right)_0 (p - p_0) + \ldots \right] d'p$$

$$< \left(\frac{\partial v}{\partial p}\right)_0 \cdot \tfrac{1}{2} (\Delta p)^2.$$

Now $\left(\frac{\partial v}{\partial p}\right)_0$ is negative. Hence

$$[(\Delta + \Delta')\zeta]_{t,\, p} < 0.$$

4. The Heat Function. We shall now prove that the variational conditions

$$(\Delta\chi)_{\eta,\, p} \geqq 0 \tag{8}$$

and

$$(\Delta\epsilon)_{\eta,\, v} \geqq 0 \tag{9}$$

are equivalent. These criteria are not stated by Gibbs, but clearly there must be a parallel set of criteria involving the heat function.

To prove that (8) implies (9) let us suppose there is a neighbouring state for which

$$(\Delta\epsilon)_{\eta,\, v} < 0.$$

We shall prove that this implies the existence of a neighbouring state violating (8). Hence if we know that (8) holds, (9) must also hold.

If this neighboring state is not one of uniform pressure, let the pressure equalize itself. This can only increase the entropy, and thus we have a state of the same energy and volume, and greater entropy. Now remove heat at constant volume until the original value of the entropy is restored. The energy can only decrease in the process. Hence we arrive at a new state of *uniform* pressure for which

$$(\Delta\epsilon)_{\eta,\,v} < 0.$$

Now

$$\chi = \epsilon + pv,$$

and hence in general

$$\Delta\chi = \Delta\epsilon + p\Delta v + v\Delta p + \Delta p\Delta v.$$

But in our case $\Delta v = 0$. Hence here

$$\Delta\chi = \Delta\epsilon + v\Delta p.$$

Consequently

$$\Delta\chi - v\Delta p = \Delta\epsilon < 0.$$

Now expand or compress *adiabatically.* For any such process, the *infinitesimal* change of energy $d'\epsilon$ is given by

$$d'\epsilon = -p\,d'v$$

and hence for this process

$$d'\chi = d'(\epsilon + pv) = v\,d'p,$$

whence for the *finite* change Δ'

$$\Delta'\chi = \int_{p_0}^{p_0 + \Delta' p} v\,d'p.$$

Hence

$$\Delta\chi + \Delta'\chi < v\,\Delta p - \int_{p_0 + \Delta' p}^{p_0} v\,d'p.$$

Choose the second process such that $\Delta' p = -\Delta p$, thus restoring the initial pressure. Then

$$\Delta\chi + \Delta'\chi < v\Delta p - \int_{p_0 - \Delta p}^{p_0} v\, d'p$$

$$< v_0\, \Delta p - \int_{p_0 - \Delta p}^{p_0} \left[v_0 + \left(\frac{\partial v}{\partial p}\right)_0 (p - p_0) + \ldots \right] d'p$$

$$< \left(\frac{\partial v}{\partial p}\right)_0 \cdot \tfrac{1}{2}\, (\Delta p)^2.$$

But

$$\left(\frac{\partial v}{\partial p}\right)_0 < 0.$$

Hence

$$[(\Delta + \Delta')\, \chi]_{\eta,\, p} < 0.$$

This contradicts (8), and so the imposition of (8) must imply the truth of (9). The proof of the converse may be left to the reader.

As an example of the application of this criterion we shall prove that c_p, the specific heat at constant pressure, must be positive. Divide a homogeneous specimen of the body into two equal parts, at the same pressure, and take a varied state of the same total entropy in which one part has been heated at constant pressure and the other cooled. Then by the properties of the heat function χ already established, we must have, if χ refers to unit mass,

$$\chi(\eta + \Delta\eta, p) + \chi(\eta - \Delta\eta, p) > 0,$$

since the gain of entropy of the one portion must be equal to the loss of entropy of the other.

It follows, by expansion by Taylor's theorem, that

$$\left(\frac{\partial^2 \chi}{\partial \eta^2}\right)_p > 0.$$

But since

$$d\chi = d(\epsilon + pv)$$

and

$$td\eta = d\epsilon + pdv,$$

it follows in the usual way that

$$d\chi = td\eta + vdp,$$

whence

$$\left(\frac{\partial\chi}{\partial\eta}\right)_p = t.$$

Hence

$$\left(\frac{\partial^2\chi}{\partial\eta^2}\right)_p = \left(\frac{\partial t}{\partial\eta}\right)_p = t \cdot \frac{1}{t}\left(\frac{\partial t}{\partial\eta}\right)_p = \frac{t}{c_p}.$$

It follows that

$$c_p > 0.$$

A similar argument involving the energy ϵ establishes that

$$c_v > 0.$$

5. *Physical Properties of the Thermodynamic Functions* ψ, ζ, χ. Gibbs' statement about these may be paraphrased and extended as follows (Gibbs, I, 89, 92).

If ΔQ represents the heat communicated to any system during any process in which the external work performed is ΔW, we know always that

$$\Delta Q = \Delta\epsilon + \Delta W.$$

Further, for any *infinitesimal* reversible change in which the masses of the ultimate constituents of the phase are unchanged,

$$dQ = td\eta.$$

6. *The Heat Function at Constant Pressure.* Let the system undergo a change at constant pressure, in such a way that the only external work done is work of expansion. Then

$$\Delta W = p\Delta v,$$

and so

$$\begin{aligned}\Delta\chi &= \Delta\epsilon + p\Delta v \\ &= \Delta\epsilon + \Delta W = \Delta Q.\end{aligned}$$

Thus the increase in the heat function between any two states is equal to the heat communicated when the same change is effected (reversibly or irreversibly) at constant pressure and no other external work is done. This property gives rise to the term "heat function." (Gibbs, I, 92, equation [119].) The change in the heat function is the quantity measured by any constant-pressure calorimeter. If dt is the increase in temperature in an infinitesimal change conducted at constant pressure when no other external work is performed, then

$$\frac{d\chi}{dt} = \frac{dQ}{dt},$$

whence

$$\left(\frac{d\chi}{dt}\right)_p = c_p.$$

7. *The Heat Function in General.* In *any* change, we have

$$\Delta\chi = \Delta\epsilon + \Delta(pv),$$

whence

$$\Delta\chi = \Delta Q - \Delta W + \Delta(pv).$$

It may happen that some of the intrinsic energy ϵ is converted into kinetic energy during the process, as in the expansion of a fluid through a nozzle. If q is the velocity of a typical element, then for unit mass the first law of thermodynamics must be written in the form

$$\Delta Q = \Delta(\tfrac{1}{2}q^2) + \Delta\epsilon + \Delta W,$$

whence

$$\Delta\chi = [\Delta Q - \Delta(\tfrac{1}{2}q^2) - \Delta W] + \Delta(pv)$$

or

$$\Delta(\chi + \tfrac{1}{2}q^2) = \Delta Q - \Delta W + \Delta(pv).$$

In the case of the steady rectilinear (irreversible) flow of a fluid under its own pressure gradient, we can show that

$$\Delta W = \Delta(pv).$$

Hence for adiabatic flow of this character, where $\Delta Q = 0$, we must have

$$\Delta(\chi + \tfrac{1}{2}q^2) = 0$$

or

$$\chi + \tfrac{1}{2}q^2 = \text{constant}.$$

(The relation $\Delta W = \Delta(pv)$ is easily proved by considering the work done on the moving element of fluid by the adjacent elements at the two opposite ends.)

If the fluid happens to be a perfect gas, we can obtain a simple expression for χ. For, for any fluid whatever,

$$\begin{aligned}\left(\frac{\partial\chi}{\partial p}\right)_t &= \left[\frac{\partial}{\partial p}(\zeta + t\eta)\right]_t \\ &= \left[\frac{\partial\zeta}{\partial p} + t\frac{\partial\eta}{\partial p}\right]_t \\ &= v - t\left(\frac{\partial v}{\partial t}\right)_p,\end{aligned}$$

since

$$d\zeta = d(\epsilon + pv - t\eta) = vdp - \eta dt.$$

Now, for a perfect gas, $v = t\left(\frac{\partial v}{\partial t}\right)_p$ since $pv \propto t$. Hence $\left(\frac{\partial\chi}{\partial p}\right)_t = 0$ and

$$\begin{aligned}d\chi &= \left(\frac{\partial\chi}{\partial p}\right)_t dp + \left(\frac{\partial\chi}{\partial t}\right)_p dt \\ &= c_p dt,\end{aligned}$$

or

$$\Delta\chi = \int c_p dt.$$

It follows that in the adiabatic rectilinear flow of a perfect gas from rest at temperature t_0 to motion with velocity q at temperature t, we have

$$\tfrac{1}{2} q^2 = -\int_{t_0}^{t} c_p dt.$$

The above somewhat miscellaneous calculations serve to illustrate the properties of the heat function.

8. The Work Function ψ at Constant Temperature. Let the system undergo a change at constant temperature, doing external work in any way whatever (e.g., electrically), as well as by expansion against external pressure. Then

$$\begin{aligned}\Delta\psi &= \Delta(\epsilon - t\eta)\\ &= \Delta\epsilon - t\Delta\eta,\end{aligned}$$

and as usual

$$\Delta Q = \Delta\epsilon + \Delta W.$$

If the change is reversible, $\Delta Q = t\Delta\eta$, and so in this case

$$\Delta\psi = -\Delta W,$$

or the increase in the work function is equal to the negative of the external work performed. (Gibbs, I, 89, equation [110].) Hence the name "work function."

All reversible processes connecting two states of the same temperature yield the same amount of external work, and any irreversible process connecting them yields less work. Thus the decrease in the work function gives the *maximum* amount of external work obtainable in changing from the first to the second state. We can prove this in another way, from first principles, as follows. If $\Delta' Q$ is the heat absorbed in *any* change whatever, by Clausius' inequalities we have

$$\Delta\eta \geqq \frac{\Delta' Q}{t},$$

and so here, the temperature being constant,

$$\Delta\epsilon - \Delta\psi = t\Delta\eta \geqq \Delta' Q.$$

In any change whatever, whether reversible or irreversible,

$$\Delta' Q = \Delta\epsilon + \Delta' W,$$

whence here

$$\Delta\epsilon - \Delta\psi \geqq \Delta\epsilon + \Delta' W$$

or

$$\Delta' W \leqq -\Delta\psi.$$

Thus the actual amount of external work performed, $\Delta' W$, cannot exceed $-\Delta\psi$.

Now suppose a system enclosed in a fixed volume. If it undergoes *of itself* any process whatever, at constant temperature, then necessarily

$$\Delta' W = 0,$$

whence

$$\Delta\psi \leqq 0.$$

Hence a necessary condition of equilibrium, subject to the condition of constant temperature and constant volume, is

$$(\Delta\psi)_{t,\,v} > 0.$$

A state for which all possible changes satisfy this relation will be in stable equilibrium, for it cannot undergo any change of itself. This establishes Gibbs' criterion concerning $\Delta\psi$ by an alternative method.

9. The Free Energy Function ζ at Constant Temperature and Constant Pressure. Let the system undergo a change at constant temperature and constant pressure, doing any external work whatever in the process. Then we have

$$\begin{aligned}\Delta\zeta &= \Delta(\epsilon - t\eta + pv)\\ &= \Delta\epsilon - t\Delta\eta + p\Delta v.\end{aligned}$$

But

$$\Delta Q = \Delta\epsilon + \Delta W.$$

If now the change is reversible, $\Delta Q = t\Delta\eta$, and so in this case

$$\Delta\zeta = -(\Delta W - p\Delta v).$$

Thus the decrease in ζ is equal to the excess of external work performed over the work of expansion against the external pressure. Hence the name "free energy" function.

If *any* process occurs at constant pressure and constant temperature, and if $\Delta' Q$ is the heat absorbed and $\Delta' W$ the external work performed,

$$\Delta\eta \geqq \frac{\Delta' Q}{t},$$

whence

$$\Delta\epsilon + p\Delta v - \Delta\zeta \geqq \Delta' Q;$$

also

$$\Delta' Q = \Delta\epsilon + \Delta' W.$$

Hence

$$\Delta\epsilon + p\Delta v - \Delta\zeta \geqq \Delta\epsilon + \Delta' W,$$

or

$$(\Delta' W - p\Delta v) \leqq -\Delta\zeta.$$

Thus the excess of external work performed over that of mere expansion cannot exceed $-\Delta\zeta$.

Now suppose that the system is enclosed in an environment of constant pressure and constant temperature. Then if any process occurs of itself, the only external work is that of expansion, and so

$$\Delta' W = p\Delta v.$$

Therefore

$$\Delta\zeta \leqq 0.$$

Hence a necessary condition that such a system shall be in stable equilibrium under the stated conditions is

$$(\Delta\zeta)_{p,\,t} > 0,$$

for it then cannot undergo any change of itself. This establishes Gibbs' criterion concerning $\Delta\zeta$ by an independent method.

10. *Further Illustration.* The following original example illustrates further the properties of the ψ-function.

"A system, which can perform external work in any manner, is brought *reversibly* from a temperature t_1 to a temperature $t_2 (< t_1)$ in such a way that it only gives up heat at the temperature t_2. Prove that the external work performed, ΔW, is given by

$$\Delta W = \Delta\psi + \eta_1(t_1 - t_2)$$

where $\Delta\psi$ is the *decrease* in the work function ψ between the temperatures t_1 and t_2, and η_1 is the entropy at t_1." (This is a generalisation of the similar result in the particular case $t_1 = t_2$ established above.)

We have

$$\psi_1 - \psi_2 = \epsilon_1 - \epsilon_2 - (t_1\eta_1 - t_2\eta_2)$$

$$\epsilon_1 - \epsilon_2 = \Delta\epsilon = \Delta Q + \Delta W,$$

where now ΔQ denotes the heat *given up* at t_2. Since the process is reversible and the heat is given up at t_2

$$\eta_1 - \eta_2 = \Delta Q / t_2.$$

Hence

$$\begin{aligned} \Delta W &= \Delta\psi + (t_1\eta_1 - t_2\eta_2) - t_2(\eta_1 - \eta_2) \\ &= \Delta\psi + \eta_1(t_1 - t_2). \end{aligned}$$

This result is, of course, somewhat trivial. We may, however, extend it to include irreversible processes. The following theorem may be established.

"If the system is brought by *any* process, reversible or irreversible, from the state at t_1 to the state at t_2, and not necessarily subject to the condition of only giving up heat when at temperature t_2, then the external work performed, $\Delta' W$, satisfies the inequality

$$\Delta' W \leqq \Delta W - \int_{\eta_2}^{\eta_1} (t - t_2)\, d\eta,$$

the integral being taken along the path in the (η, t) diagram actually traversed by the system and ΔW having the same meaning as above."

For, along any path whatever, if the differentials which follow denote positive increments,

$$d'Q = d'\epsilon + d'W$$

and

$$d'\eta \geqq \frac{d'Q}{t},$$

$d'Q$ denoting the heat given up at t. Hence

$$d'W \leqq - d'\epsilon + t\, d'\eta.$$

Since $d'\epsilon$ and $d'\eta$ are the actual increments in the functions ϵ and η along the path, we may replace them by $d\epsilon$ and $d\eta$. Now

$$d\psi = d\epsilon - t d\eta - \eta dt.$$

Hence

$$d'W \leqq -d\psi - \eta dt.$$

Integrating,

$$\begin{aligned} \Delta' W &\leqq \Delta\psi - \int_{t_1}^{t_2} \eta dt \\ &\leqq \Delta\psi + (t_1\eta_1 - t_2\eta_2) - \int_{\eta_2}^{\eta_1} t d\eta \\ &\leqq \Delta W + t_2\,(\eta_1 - \eta_2) - \int_{\eta_2}^{\eta_1} t d\eta \end{aligned}$$

on using the result of the first part. Hence

$$\Delta' W \leqq \Delta W - \int_{\eta_2}^{\eta_1} (t - t_2)\, d\eta.$$

Since $\Delta Q > 0$ it follows that $\eta_1 > \eta_2$. If $t \geqq t_2$ throughout the process, the integral is positive whether or not t is a single-valued function of η during the process (i.e., whether or not the system always has the same temperature at intermediate stages at which the entropy takes the same value). Consequently

$$\Delta' W \leqq \Delta W .$$

It follows that ΔW is the *maximum* amount of external work that can be obtained by processes in which the temperature of the system does not fall below t_2. That is, the maximum work is obtained when all the heat is given up reversibly at temperature t_2, and the amount of this work is

$$\Delta\psi + \eta_1 (t_1 - t_2),$$

$\Delta\psi$ being the *decrease* in the work-function. This extends the physical significance of the work-function to processes of non-constant temperature.

The absolute value η_1, of the entropy appears to occur in this expression; but it must be remembered that the absolute value of the entropy occurs also in the definition of ψ. The same constants used in fixing the entropy η, must be employed in the entropy-values used in tracing the changes in ψ.

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THE PHASE RULE AND HETEROGENEOUS EQUILIBRIUM

[*Gibbs, I, pp. 96–100*]

GEORGE W. MOREY

I. Introduction

Treatises on the Phase Rule usually deal with heterogeneous equilibrium from a purely geometrical point of view, making use of the familiar equation, $F = n + 2 - r$, in which F is the number of degrees of freedom, n the number of components, and r the number of phases, as a qualitative guide, and depending on the Theorem of Le Chatelier for determining the effect of change of conditions on the equilibrium. It is unfortunate that the subject has been developed in this manner, instead of by the direct application of the equations which were developed by Gibbs. The Phase Rule itself is but an incidental qualitative deduction from these equations, and the justification of the geometrical methods is their derivation as projections of the lines and surfaces "of dissipated energy," painstakingly exemplified* by Gibbs. While in the first portion of the "Equilibrium of Heterogeneous Substances" the actions of gravity, electrical influences, and surface forces are excluded from consideration, these restrictions are later removed, thus rendering unnecessary the various "extended" Phase Rules which have been proposed to remedy this supposed defect.

II. Equation [97] and the Phase Rule

1. *Equation* [*97*]. The Phase Rule may be derived from Gibbs' fundamental conditions for equilibrium [15–21], but Gibbs' own treatment is intimately connected with his equation [97]

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* Equilibrium of Heterogeneous Substances, Gibbs, I, 118 et seq.

$$vdp = \eta dt + m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n, \qquad (1)\ [97]$$

in which v and η refer to the volume and entropy of $m_1 + m_2 \ldots + m_n$ units of the phase considered, p and t to the pressure and temperature, and μ to "the potential for the substance in the homogeneous mass considered." The chemical potential, μ, is defined by the equations

$$\mu_1 = \left(\frac{d\epsilon}{dm_1}\right)_{\eta,\,v,\,m} = \left(\frac{d\psi}{dm_1}\right)_{t,\,v,\,m} = \left(\frac{d\chi}{dm_1}\right)_{\eta,\,p,\,m} = \left(\frac{d\zeta}{dm_1}\right)_{t,\,p,\,m}, \qquad (2)\ [104]$$

in which ϵ, ψ, χ, and ζ refer, respectively, to the energy and the three Gibbs' thermodynamic functions defined by the equations

$$\psi = \epsilon - t\eta, \qquad (3)\ [87]$$

$$\chi = \epsilon + pv, \qquad (4)\ [89]$$

$$\zeta = \epsilon - t\eta + pv. \qquad (5)\ [91]$$

The first of these, ψ, is the quantity defined by Helmholtz* as the free energy, and commonly designated by that name in Continental writings; the second, χ, the quantity variously known as heat content, enkaumy and enthalpy;† the third, ζ, the quantity called free energy by Lewis.‡ The definition of μ is evidently symmetrical with respect to ϵ, ψ, χ and ζ, and it should not be considered as specially related to any one of these quantities.

2. Derivation of the Phase Rule. Equation (1) [97] expresses a necessary relationship at equilibrium between the intensive properties of any phase, and this relationship itself is a consequence of the fundamental condition for equilibrium, namely, that in an isolated system the entropy shall be a maximum for the given energy and volume. The concept of phase, and the derivation of the Phase Rule, result from the application of equation (1) [97] to the consideration of "the different homogeneous bodies which can be formed out of any set of component substances." "It will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition or state different *phases* of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend on passive resistances to change, we shall call *coexistent.*

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* Helmholtz, *Sitzb. preuss. Akad. Wiss.* 1, 22 (1882).

† The term enthalpy, proposed by H. Kamerlingh Onnes (Leiden Comm. No. 109 (1909), p. 3) is, in the author's opinion, the best for the designation of this important quantity.

‡ The thermodynamic quantities of Gibbs refer to a total mass of $(m_1 + m_2 + \ldots m_n)$ units of the phase or system in question, while some of the names subsequently applied to the Gibbs functions refer by definition to a gram molecular weight. That, for example, is the difference between Gibbs' ζ and Lewis' free energy.

"If a homogeneous body has n independently variable components, the phase of the body is evidently capable of $n + 1$ independent variations." This follows from the fact that there are $n + 2$ independent variables, pressure, temperature, and the n quantities μ_1, μ_2, . . . μ_n connected by an equation of the form of (1) [97]. "A system of r coexistent phases, each of which has the same n independently variable components is capable of $n + 2 - r$ variations of phase," or degrees of freedom, F. "For the temperature, the pressure, and the potentials for the actual* components have the same values in the different phases, and the variations in these quantities are by [97] subject to as many conditions as there are different phases. Therefore, the number of independent variations in the values of these quantities, i.e., the number of independent variations of phase of the system, will be $n + 2 - r$."

"Hence, if $r = n + 2$, no variation in the phases (remaining coexistent) is possible. It does not seem probable that r can ever exceed $n + 2$. An example of $n = 1$ and $r = 3$ is seen in the coexistent solid, liquid, and gaseous forms of any substance of invariable composition. It seems not improbable that in the case of sulphur and some other simple substances there is more than one triad of coexistent phases; but it is entirely improbable that there are four coexistent phases of any simple substance.* An example of $n = 2$ and $r = 4$ is seen in a solution of a salt in water in contact with vapor of water and two different kinds of crystals of the salt." Coexistence of $r = n + 2$ phases gives rise to an invariant equilibrium, and such a coexistence is frequently called an invariant point. Invariant points are also referred to by the number of phases present; for example, a triple point in a one-component system, quadruple point in a two-component system, etc.

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* The distinction between "actual" and "possible" components need not be discussed in this place. See Gibbs, I, 66.

When $r = n + 1$, there are $n + 1$ equations of the form of (1) [97], one for each of the coexisting phases, and the system has one degree of freedom. We may eliminate n of the $n + 2$ independent variables, giving an equation between the two remaining. If the quantities $d\mu_1, d\mu_2, \ldots d\mu_n$ are eliminated by the usual method of cross multiplication, we obtain a linear equation between the changes in pressure and temperature, which for the general case takes the form

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & m_1' & m_2' & \ldots & m_n' \\ \eta'' & m_1'' & m_2'' & \ldots & m_n'' \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdots & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdots & \cdot\cdot \\ \eta^n & m_1^n & m_2^n & \ldots & m_n^n \end{vmatrix}}{\begin{vmatrix} v' & m_1' & m_2' & \ldots & m_n' \\ v'' & m_1'' & m_2'' & \ldots & m_n'' \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdots & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdots & \cdot\cdot \\ v^n & m_1^n & m_2^n & \ldots & m_n^n \end{vmatrix}}. \qquad (6)\ [129]$$

We shall develop in detail the application of this equation to several types of systems.

III. Application of Equation [97] to Systems of One Component

3. The Pressure-Temperature Curve of Water. A simple case of heterogeneous equilibrium is that of a one-component system, such as water, in which the liquid coexists with its own vapor at a series of pressures and temperatures. There are two equations of the form of (1) [97], one for the vapor and one for the liquid. If we denote vapor and liquid by the indices v and l, and use, as we shall hereafter, the capital letters V and H (capital eta) for total volume and total entropy, respectively, these equations are

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* For an extended discussion of the possibility of the coexistence of more than $n + 2$ phases, see R. Wegscheider, *Z. physik. Chem.*, **43**, 93 (1903) et seq.; A. Byk, ibid., **45**, 465 (1903) et seq.

$$V^v dp = \mathrm{H}^v dt + m^v d\mu,$$

and

$$V^l dp = \mathrm{H}^l dt + m^l d\mu.$$

It will be remembered, from the derivation of these equations, that the quantities V and H refer to the total volume and total entropy of the mass considered; in this case, where there is only one component, to the total volume and entropy of the m grams contained in each phase. If we divide each equation through by the mass m, they take the form

$$\begin{aligned} v^v dp &= \eta^v dt + d\mu, \\ v^l dp &= \eta^l dt + d\mu, \end{aligned}$$

in which the lower-case letters are used to denote specific volume and specific entropy, as opposed to the total volume and total entropy, denoted by the capital letters. We can eliminate $d\mu$ between these equations by subtraction, giving us

$$(v^v - v^l)dp = (\eta^v - \eta^l)dt$$

or

$$\frac{dp}{dt} = \frac{\eta^v - \eta^l}{v^v - v^l}.$$

Since $d\mathrm{H} = dQ/t$, which on integration at constant temperature yields $\Delta\mathrm{H} = \frac{\Delta Q}{t}$, this reduces to the usual Clausius-Clapeyron equation

$$\frac{dp}{dt} = \frac{\Delta Q}{t\,(v^v - v^l)}.$$

It will be of interest to consider the detailed application of the equation

$$\frac{dp}{dt} = \frac{\eta^v - \eta^l}{v^v - v^l}$$

to the pressure-temperature curve of water.

* The thermodynamic properties of water are known to a considerable degree of precision, and tables giving the specific entropy and specific volume of water and steam are in common use by engineers. In such tables it is customary to take the specific entropy of liquid water at zero degrees centigrade as zero, but since we are always dealing with differences in entropy this is immaterial. Absolute values of entropy are not determinable; to determine absolute values of entropy we would have to know the value of the entropy at absolute zero,† and its variation with temperature from the absolute zero up, and we do not possess the necessary data for this. Herein lies one of the reasons for the entropy concept being a difficult one to grasp; we are not able to measure entropy directly as we are able to measure the other quantity factors, volume and mass. For practical purposes, however, this is not material, since we are always dealing with entropy differences. In Fig. 1 are shown plotted the specific entropy of liquid water and the specific entropy of saturated water vapor from zero to 200°C., the specific volume of water vapor at the saturation pressure in the same temperature range, and the pressure-temperature curve of the equilibrium, liquid + vapor. Since the slope of the p-t curve is determined by the difference in entropy between vapor and liquid, it is immaterial whether the entropy of the

liquid at 0°C. is taken as zero or some other value. The entropy of the vapor is greater than that of the liquid by the entropy of vaporization, that is, the heat of vaporization divided by the absolute temperature. In the case of the volume, only the specific volume of the vapor is plotted, as that of the liquid is so small that it cannot be shown on the scale of the diagram. Let us now consider some actual values.

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* From this point to the end of section (11), p. 251, the text is taken, with some omissions, alterations and additions, from the author's article, *Jour. Franklin Inst.*, **194**, 439–450 (1922); sections (16) to (23) inclusive (except (18) and (22)) are taken in like manner from the same article, pp. 450–460.

† Absolute values of entropy may be calculated for many substances by the use of the so-called Third Law of Thermodynamics, a principle whose validity has not been completely demonstrated.

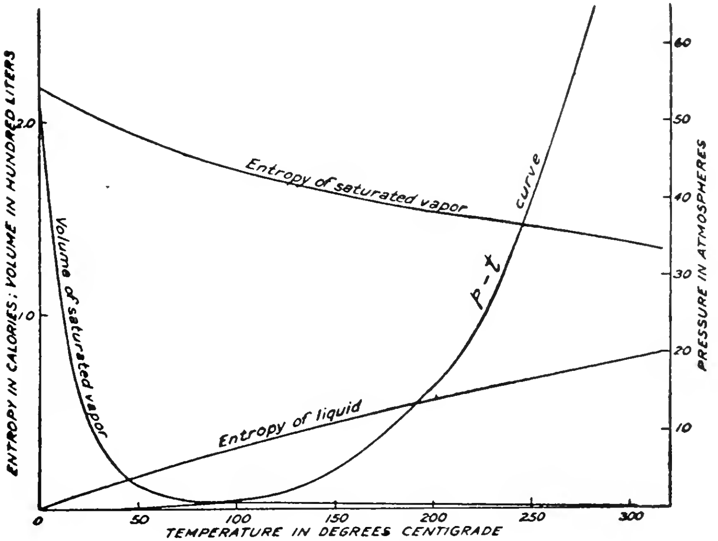

FIG. 1. The specific entropy of liquid water and of saturated water vapor, the specific volume of saturated water vapor, and the vapor pressure of water, plotted against temperature.

At zero degrees centigrade, if the entropy of the liquid is zero, that of the vapor is 2.18 calories. The specific volume of water vapor in equilibrium with liquid at zero degrees is 206 liters per gram; it is evident that the volume of the liquid, 1 cc., is negligible in comparison. In the equation

$$\frac{dp}{dt} = \frac{\eta^v - \eta^l}{v^v - v^l},$$

the terms must all be of the same kind; if the slope of the *p-t* curve is given in atmospheres per degree, and the volume in liters, the entropy must be expressed in liter-atmospheres instead of in calories. The factor for this conversion is 0.0413; inserting the above values in the equation, we get

$$dp/dt = (2.180 \times 0.0413)/206 = 0.00044 \text{ atm. per degree;}$$

the corresponding experimental value is the same. At 50° the values are

$$\frac{dp}{dt} = \frac{(1.928 - 0.168)\,(0.0413)}{(12.02 - 0.001)} = 0.0060.$$

Again the experimental value is the same, and the volume of the liquid is still negligible. At 100°, the corresponding quantities are

$$\frac{dp}{dt} = \frac{(1.756 - 0.312)\,(0.0413)}{(1.209 - 0.001)} = 0.0357,$$

agreeing exactly with experiment. At this temperature the volume of the liquid amounts to less than one-tenth of one per cent of the total volume; the value of *dp/dt* is increasing with increasing temperature, and the explanation is evident from an inspection of the entropy and volume curves. As the temperature is increased the entropy of the vapor diminishes, that of the liquid increases, hence the difference decreases as the temperature increases. The numerator, the entropy of vaporization, is therefore diminishing, but its decrease is more than offset by the decrease in the denominator taking place at the same time because the increasing vapor pressure increases the density of the vapor, hence decreasing its specific volume. In the interval from zero to 10° the numerator decreases to 95.6 per cent of its value at zero, while the denominator decreases to only 51.5 per cent of its value at zero. The difference does not remain so marked, but for the interval 90–100° the values are 96 per cent and 70.9 per cent, respectively, and for the interval 190–200°, 96.1 per cent and 81.4 per cent, respectively. Application of the two equations of the form of (1) [97] to the univariant equilibrium, liquid + vapor, in the one-component system, water, shows us that not only does the pressure increase with increasing temperature, but the rate of increase also increases. The p-t curve is accordingly concave upward, and the slope continues to increase. As the critical point of water is approached, the difference between the properties of liquid and vapor diminishes rapidly, and vanishes at the critical temperature. Hence the equation for the p-t curve becomes indeterminate, and the vapor pressure curve ends.

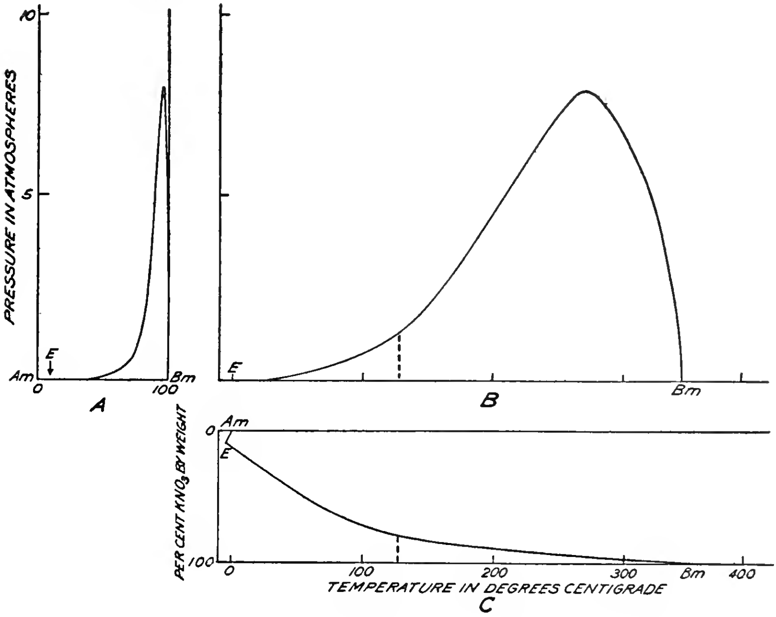

FIG. 2. The binary system, H_2O-KNO_3. Diagrams A, B, and C are the projections of the curve representing the three-phase equilibrium, vapor + saturated solution + solid KNO_3, in the solid p-t-x model on the pressure-composition (p-x), pressure-temperature (p-t), and temperature-composition (t-x) planes, respectively.

IV. Application of Equation [97] to Systems of Two Components

4. Application of the Phase Rule to a System in Which No Compounds Are Formed. H_2O-KNO_3. We will now consider the case of a simple binary system, choosing the system, water-KNO_3, as an illustration. The relationship between pressure, temperature, and composition is shown in Fig. 2, A, B, and C, which may be regarded as the projections of the solid *p-t-x* model on the *p-x*, *p-t*, and *t-x* planes, respectively. It should be noted that in referring to these projections, and to the similar ones in the following figures, their conventional designation in chemical literature has been followed, instead of the convention in mathematics that the symbols shall be in the order abscissa, ordinate; x, y. The system, H_2O-KNO_3,* does not show liquid immiscibility, nor are solid hydrates formed, so there are four possible phases in the system; one vapor phase, one liquid phase and two solids, ice and solid KNO_3. Coexistence of four phases in a two-component system gives us four equations of the type of (1) [97] between the four unknowns, pressure, temperature, and the two chemical potentials, so the system is completely determined. The four phases can only coexist at one temperature and one pressure, that is, at the invariant point, often called the cryohydrate when one component is water. The invariant point can be considered as the intersection of four curves representing univariant equilibria, each of which equilibria will contain three of the phases which coexisted at the invariant point. We can have the four combinations: ice + solution + vapor, ice + potassium nitrate + vapor, ice + potassium nitrate + solution, and potassium nitrate + solution + vapor. Consider each of these curves in detail, starting with the last, the solubility curve of potassium nitrate in water.

5. *Application of Equation [97] to a System in Which No Compounds Are Formed.* H_2O-KNO_3. In the univariant equilibrium, potassium nitrate + solution + vapor, there is only one phase of variable composition, the solution. Since potassium nitrate is not volatile at temperatures we are considering, the vapor phase is pure water; since potassium nitrate forms neither hydrates nor solid solutions with water, the solid phase is pure potassium nitrate. Let us now apply equation (1) [97] to this univariant equilibrium. In the derivation of equation (1) [97],

$$Vdp = \mathrm{H}dt + m_1 d\mu_1 + m_2 d\mu_2$$

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* The circumstance that an inversion takes place in KNO_3 at 127.8° is ignored, as not being pertinent to the points under consideration.

for a two-component system, composition was expressed as the total mass m_1 and m_2 of the substances present, and volume and entropy as total volume and total entropy. For some purposes this is the most convenient form, but for our present discussion it is more convenient to express composition as weight per cent potassium nitrate. Since we have $m_1 + m_2$ grams of the two components water and potassium nitrate, respectively, if we divide through by $m_1 + m_2$ we shall get

$$\frac{V}{m_1 + m_2}\,dp = \frac{\mathrm{H}}{m_1 + m_2}\,dt + \frac{m_1}{m_1 + m_2}\,d\mu_1 + \frac{m_2}{m_1 + m_2}\,d\mu_2.$$

The coefficient of the first term, the total volume divided by the total number of grams of material, is evidently the specific volume of the phase. Similarly, the coefficient of the second term is the specific entropy. The fractions

$$\frac{m_1}{m_1 + m_2} \text{ and } \frac{m_2}{m_1 + m_2}$$

are the weight fractions of the components H_2O and KNO_3, respectively, and if we represent the weight fraction of KNO_3 by x, that of H_2O will be $(1 - x)$. The equation now is

$$v\,dp = \eta\,dt + (1 - x)d\mu_1 + x\,d\mu_2, \tag{7}$$

in which v and η are specific volume and specific entropy. We will have three such equations, one for the vapor, denoted by the superscript v, one for the liquid, denoted by the superscript l, and one for the solid, denoted by the superscript s. From these equations we may eliminate $d\mu_1$ and $d\mu_2$ by the usual methods of cross-multiplication, giving the equation

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) - \dfrac{x^v - x^l}{x^s - x^l}(\eta^s - \eta^l)}{(v^v - v^l) - \dfrac{x^v - x^l}{x^s - x^l}(v^s - v^l)}. \tag{8}$$

*6. The Equilibrium, KNO_3 + Solution + Vapor.** At the cryohydrate point the weight fraction KNO_3 is 0.021; since the vapor is pure water, its weight fraction of KNO_3 is zero, and that of the solid phase is unity. Substituting these values, we get

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* The data for the system, H_2O-KNO_3, are taken in part from Landolt-Börnstein, *Physikalisch-chemische Tabellen*, 1912; in part from unpublished data by F. C. Kracek and G. W. Morey.

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) + \dfrac{0.021}{0.979}(\eta^s - \eta^l)}{(v^v - v^l) + \dfrac{0.021}{0.979}(v^s - v^l)}.$$

The coefficient of the second term in both numerator and denominator is a fractional coefficient. Without an actual determination of the entropy of any phase, certain definite conclusions can be drawn. In the numerator, we have the entropy differences: (vapor − liquid), a positive quantity, and (solid − liquid), a negative quantity. The former is always several times the latter; in the case of this dilute solution their ratio is probably not very different from the ratio of the entropy of vaporization of water to the entropy of fusion of KNO_3, which is of the order of magnitude of 20 to 1. The first term predominates, and the numerator is a positive quantity of the order of magnitude of the entropy of vaporization of water at zero degrees, or a little less than 2.18. In the denominator the term affected by the fractional coefficient, the difference in specific volume of liquid and solid, is negative and is itself very small. The first term, the volume difference (vapor-liquid), is comparatively enormous; at the cryohydrate temperature and pressure it is even larger than the volume difference in pure water at its freezing point, 206 liters per gram. The slope of the pressure-temperature curve is at the beginning close to that of pure water; that of pure water is concave upward, owing to the denominator decreasing in value more rapidly than the numerator, and the same is true in this case. The pressure-temperature curve of all systems containing a volatile component at low pressure will show a similar initial upward concavity, owing to the rapid decrease in the specific volume of the vapor phase with increasing pressure.

As the temperature is raised, the fraction of KNO_3 in the liquid increases, while the composition of the other phases remains the same. The specific entropy of the vapor continually decreases; that of the solid increases, as does that of the liquid. The first term in the numerator consequently decreases, the second increases, and the coefficient of the second term also increases; since the first term is positive, while the second is negative, the numerator is a continually decreasing positive quantity. The denominator is decreasing at a progressively slower rate. As the temperature is raised these effects continue, until a temperature is reached at which the rate of decrease of the numerator becomes equal to that of the denominator, and the curve has a point of inflection. After this it is no longer concave upward, but is concave downward, as the vapor pressure of the saturated solution is still increasing with the temperature, but at a diminishing rate. The temperature of this point of inflection is approximately 205°, and the pressure is about 5.3 atmospheres.

The determination of the solubility curve of KNO_3 in H_2O is a simple matter at temperatures below 100°. As long as the vapor pressure remains less than one atmosphere, we can shake up solid and liquid in a thermostat until equilibrium is reached, suck out a sample of the supernatant liquid through a filter, and determine the composition by analysis. After the pressure has exceeded one atmosphere, other methods must be employed. Of course, if a mixture containing an excess of KNO_3 is heated in an open vessel, when the vapor pressure reaches one atmosphere the solution will begin to boil, and will evaporate to dryness. But if the mixture be heated in a closed tube, from which the water cannot evaporate, the solubility curve will be continuous until the mixture is entirely liquid; the temperature at which the saturated solution boils at a pressure of one atmosphere is not a significant point on the solubility curve. From this point of view there is no distinction between a solubility curve and a melting-point curve, and the curve EB_m can be regarded either as the solubility curve of KNO_3 in H_2O or as the melting-point curve of H_2O-KNO_3 mixtures. The first to realize this fact was Guthrie* in 1884, and the system, H_2O-KNO_3, was one of those that he studied. He sealed mixtures in closed tubes and observed the temperature at which the crystals disappeared.

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* Guthrie, *Phil. Mag.*, **18**, 117 (1884).

As the temperature is raised past the point of inflection of the *p-t* curve, the KNO_3 content of the liquid increases and the coefficient of the second term in the numerator increases correspondingly. At 115°, the boiling point of the saturated solution, the ratio $x^l/(1 - x^l)$ is about 2.5; at the point of inflection, about 4. As this coefficient continues to increase, the numerator decreases more and more rapidly, and the value of dp/dt decreases; but, as it is still positive, the pressure continues to increase with temperature. With a little further increase in temperature, the ratio $x^l/(1 - x^l)$ becomes such that the entire second term equals the first term, and the difference is zero; the numerator is now zero, so dp/dt is zero, and the curve has a horizontal tangent. Since at this point

$$(\eta^v - \eta^l) + \frac{x^l}{1 - x^l}(\eta^s - \eta^l) = 0,$$

it follows that

$$\frac{x^l}{1 - x^l} = -\frac{\eta^v - \eta^l}{\eta^s - \eta^l}.$$

The ratio of the entropy difference (vapor-liquid) to the entropy difference (solid-liquid) is equal to the ratio of KNO_3 to water in the saturated solution; the saturated solution at this point contains about 95.3 per cent KNO_3, so this ratio is approximately 95.3/4.7, or 20. The entropy of the water vapor at this temperature and pressure can be obtained from steam tables, that of KNO_3 from specific heat data, and the entropy of the liquid can accordingly be calculated. It should be remembered that we are here dealing with entropy differences, not absolute entropy, and when we take off the entropy of the steam from a steam table we must remember that the assumption is made in the steam table that the entropy of liquid water at its freezing point is zero.

7. The Maximum Pressure of the Equilibrium, KNO_3 + Solution + Vapor. The point of maximum pressure is found at a KNO_3 content of about 95.3 per cent, a temperature of about 266°, and a pressure of about 7.9 atmospheres. Our equation is

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) + \dfrac{0.953}{1 - 0.953}(\eta^s - \eta^l)}{(v^v - v^l) + \dfrac{0.953}{0.047}(v^s - v^l)},$$

and the numerator is zero because the negative entropy difference (solid-liquid), multiplied by the ratio $x^l/(1 - x^l)$ is equal to the positive entropy difference (vapor-liquid). On further increase in temperature x continues to increase, the negative second term becomes larger than the positive first term, and the numerator becomes negative. The denominator is still positive, so the *p-t* curve has a negative slope; pressure decreases with increasing temperature. On further increase in temperature, the numerator continues to become more strongly negative, until at the melting point of pure KNO_3 it is the entropy difference (solid-liquid) for KNO_3.

8. The Maximum Temperature of the Equilibrium, KNO_3 + Solution + Vapor. The changes which have been taking place in the denominator will now be considered. The specific volume of the vapor phase at all points is much larger than that of any other phase, its smallest value at the maximum pressure being about 100 cc. per gram. As the pressure decreases from this point, the specific volume of the vapor increases; the effect of this is merely to alter the rate of decrease of pressure which takes place from this point. But as the liquid phase approaches KNO_3 in composition, the amount of water becoming very small, the second term in the denominator becomes of importance. The specific volume difference between fused and solid KNO_3 is but a few tenths of a cubic centimeter; when the water content is only 0.1 per cent, the negative volume difference (solid-liquid) is multiplied by the ratio 999/1, and at 0.01 per cent water, by 10,000. As the water content decreases, the coefficient of the second term in the denominator, $(v^s - v^l)$, increases rapidly, the denominator approaches zero, and the slope of the *p-t* curve, dp/dt, becomes infinite. At this one point the curve is vertical; on further increase in temperature the curve again has a positive slope. In a system of the type, H_2O-KNO_3, the experimental realization of this portion of the curve would be extremely difficult and we will not consider it further at present, except to point out that at zero water content the equation becomes

$$\frac{dp}{dt} = \frac{\eta^s - \eta^l}{v^s - v^l},$$

which is the equation of the tangent to the melting-point curve of pure KNO_3. The *p-t* curve of the saturated solutions is therefore tangent at its end to the melting-point curve of KNO_3, the curve showing the change in melting point of potassium nitrate with pressure. This type of equilibrium will be considered later.

9. The Second Boiling Point. We have seen that a melting-point or solubility curve of the system, H_2O-KNO_3, extends from the cryohydrate *E* to the melting point of pure KNO_3, and have followed the change in vapor pressure with composition in detail. We have therefore correlated the temperature-composition or solubility curve with the pressure-temperature curve. One curve gives the change with the temperature in the composition of the liquid in equilibrium with solid and vapor, the other gives the change with temperature in the vapor pressure of the saturated solution. One other pair of the three variables, composition of the liquid, temperature, and pressure, can be considered, namely, the change in vapor pressure of the saturated solution with composition. This is the pressure-composition curve; from it we see that the vapor pressure at first increases with decreasing water content of the saturated solutions, reaches a maximum at a small H_2O content, then decreases rapidly with further diminution of the water content, until at its end-point at pure KNO_3 the vapor pressure is that of the triple point of KNO_3. We are all familiar with the fact that as the water content of the saturated solution decreases with increasing temperature the vapor pressure increases, until at the boiling point of the solution the pressure of the atmosphere is reached. But there are two saturated solutions whose vapor pressure is one atmosphere; one has a water content of 29 per cent, the other of only one per cent. At the first boiling point, addition of heat causes the solution to evaporate, liquid changing into solid and vapor. At the boiling point at higher temperature, called by Roozeboom, who discovered it, the second boiling point, the solution boils on cooling. At the second boiling point, the liquid changes into solid and vapor with evolution of heat. If a melt of KNO_3, saturated at its melting point with water, be quickly cooled, it will be seen to boil suddenly and violently, and at the same time to solidify. This second boiling point has been observed in many systems,* including silicate systems at high temperatures, and the phenomenon has been made the basis of a theory of volcanism,† which has been applied successfully to the activity of Mt. Lassen, California.‡

10. The Equilibrium, Ice + Solution + Vapor. Of the four univariant equilibria which proceed from the invariant point we have considered but one, namely, the univariant equilibrium, solid KNO_3 + solution + vapor. The univariant equilibrium, ice + solution + vapor, is a second one in which we have both liquid and vapor, and in this case solid and vapor have the same composition. Our equation (8) becomes

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) - \dfrac{x^v - x^l}{x^s - x^l}(\eta^s - \eta^l)}{(v^v - v^l) - \dfrac{x^v - x^l}{x^s - x^l}(v^s - v^l)}$$

and, since $x^v = x^s = 0$,

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) - \dfrac{0 - x^l}{0 - x^l}(\eta^s - \eta^l)}{(v^v - v^l) - \dfrac{0 - x^l}{0 - x^l}(v^s - v^l)} = \frac{\eta^v - \eta^s}{v^v - v^s}.$$

But this equation refers to the vapor-pressure curve of ice; all terms relating to the liquid have disappeared. This is a general relation; whenever any two phases in a binary system have the same composition the pressure-temperature relations become those of these two phases, without reference to the composition of the other phase present.

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* H. W. Bakhuis Roozeboom, *Proc. Roy. Soc. Amsterdam,* **4,** 371 (1901).

† G. W. Morey, *J. Wash. Acad. Sci.,* **12,** 219 (1922).

‡ A. L. Day and E. T. Allen, Carnegie Inst. Wash., Publ. No. 360 (1925). A. L. Day, *J. Franklin Inst.,* **200,** 161 (1925).

11. The Equilibria, Ice + KNO_3 + Vapor, and Ice + KNO_3 + Solution. The preceding univariant equilibria have been formed from the invariant equilibrium, ice + KNO_3 + solution + vapor, by the disappearance of ice or of KNO_3, respectively. Two others can be obtained, by the disappearance of liquid or of vapor. In case the liquid disappears, we have left ice + KNO_3 + vapor, and the *p-t* curve of this equilibrium will coincide with the vapor-pressure curve of ice, and from the invariant point will go to lower pressure and lower temperature. In case the vapor disappears we have the condensed system, ice + KNO_3 + liquid, and the curve gives the change in eutectic (cryohydrate) composition with pressure. The equation of this curve* is

$$\frac{dp}{dt} = \frac{(\eta^{ice} - \eta^{l}) - \dfrac{x^{ice} - x^{l}}{x^{KNO_3} - x^{l}}(\eta^{KNO_3} - \eta^{l})}{(v^{ice} - v^{l}) - \dfrac{x^{ice} - x^{l}}{x^{KNO_3} - x^{l}}(v^{KNO_3} - v^{l})},$$

and since $x^{ice} = 0$, $x^{KNO_3} = 1$, and $x^{l} = 0.021$, this becomes

$$\frac{dp}{dt} = \frac{(\eta^{ice} - \eta^{l}) + \dfrac{0.021}{0.979}(\eta^{KNO_3} - \eta^{l})}{(v^{ice} - v^{l}) + \dfrac{0.021}{0.979}(v^{KNO_3} - v^{l})}.$$

Here again the entropy and volume changes of the water are the predominating factors; since the entropy difference is positive and the volume difference, in the exceptional case of water, negative, the *p-t* curve of this equilibrium has a negative slope. But in this case, as in all condensed systems, the slope is very steep; the numerator is of the order of magnitude of 0.3 cal. or 0.012 liter-atmospheres; the denominator is of the order of magnitude of 0.1 cc., or 0.0001 liters. The value of dp/dt is thus about $-0.012/0.001$, or 120 atmospheres per degree; the curve will be almost vertical. In other words, pressure, as compared with temperature, has, as a rule, but little effect on the equilibrium temperature and composition.

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* This is the equation of the tangent to the curve; but it is convenient to refer to it as the equation of the curve itself, and need not cause confusion.

12. Derivation of an Equation in Which the Argument Is Pressure, Temperature, and Composition. It will be of interest to correlate the solubility (t-x) curve more closely with the p-t curve.* The p-t curve gives the change of vapor pressure with temperature along the three-phase curve, representing coexistence of vapor, liquid (saturated solution), and solid, and the equation used in its discussion contained pressure and temperature as expressed variables. The t-x curve represents the change with temperature of the weight fraction x of the second component in the saturated solution along the same curve, and for its discussion it is useful to have an equation containing temperature and composition as expressed variables. Applying (1) [97] in the form of equation (7) to two coexisting phases, denoted by single and double accents, and eliminating $d\mu_1$, gives

$$[v'(1 - x'') - v''(1 - x')]dp = [\eta'(1 - x'') - \eta''(1-x')]dt + (x' - x'')d\mu_2. \tag{9}$$

But μ is a function of pressure, temperature, and composition, so we may write

$$d\mu_2 = \left(\frac{\partial \mu_2}{\partial p}\right) dp + \left(\frac{\partial \mu_2}{\partial t}\right) dt + \left(\frac{\partial \mu_2}{\partial x}\right) dx. \tag{10}$$

From the equation

$$d\epsilon = td\mathrm{H} - Vdp + m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n, \qquad (11)\ [12]$$

it follows that

$$\frac{\partial \mu_2}{\partial p} = \frac{\partial V}{\partial m_2}, \text{ and } \frac{\partial \mu_2}{\partial t} = -\frac{\partial \mathrm{H}}{\partial m_2},$$

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* Cf. footnote on page 257.

which give the rate of change of total volume and of total entropy, respectively, on addition of m_2. Since

$$V = (m_1 + m_2)v, \qquad \frac{\partial V}{\partial m_2} = v - (1 - x)\frac{\partial v}{\partial x}$$

and, similarly,

$$\frac{\partial H}{\partial m_2} = \eta - (1 - x)\frac{\partial \eta}{\partial x}.$$

Substituting these values of $\frac{\partial \mu_2}{\partial p}$ and $\frac{\partial \mu_2}{\partial t}$ in (10), inserting this value of $d\mu_2$ in (9) and rearranging, gives

$$\left[v' - v'' - (x' - x'')\frac{\partial v''}{\partial x''}\right] dp = \left[\eta' - \eta'' - (x' - x'')\frac{\partial \eta''}{\partial x''}\right] dt + \frac{x' - x''}{1 - x''}\frac{\partial \mu_2}{\partial x''} dx''. \tag{12}$$

This is a general equation* for the equilibrium between two phases in a binary system. The term $\frac{\partial \mu_2}{\partial x''}$ can in general be evaluated only from experimental data; indeed, the whole of chemical equilibrium is contained in the evaluation of this term. Gibbs has indicated the form it takes for dilute solutions, and has shown that it is necessarily† positive for stable phases.

13. Derivation of an Equation Applying to the Solubility (*t-x*) *Curve.* Equation (12) can be written in the form

$$\Delta v^{12}\, dp = \Delta \eta^{12}\, dt + \frac{x' - x''}{1 - x''}\frac{\partial \mu_2}{\partial x''} dx'', \tag{13}$$

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* This equation can be derived in a number of different ways; the introduction of equation (1) [97] is not necessary nor is it the most convenient way. It is used here as being more in harmony with the general mode of treatment. Cf. E. D. Williamson and G. W. Morey, *J. Am. Chem. Soc.*, **40**, 49 (1918).

† Gibbs, I, 112. The proof refers to $\frac{\partial \mu_2}{\partial m_2}$ but it is easily shown that if this is positive $\frac{\partial \mu_2}{\partial x''}$ must be positive also.

in which Δv^{12} and $\Delta\eta^{12}$ have been substituted for

$$\left[v' - v'' - (x' - x'')\frac{\partial v''}{\partial x''}\right] \text{ and } \left[\eta' - \eta'' - (x' - x'')\frac{\partial \eta''}{\partial x''}\right],$$

respectively. This applies to any two-phase equilibrium; if we have in addition a third phase, denoted by triple accents, we have another equation of the same form. Elimination of dp between the two equations and solving for $\frac{dt}{dx''}$, gives

$$\frac{dt}{dx''} = -\frac{1}{1 - x''}\frac{\partial \mu_2}{\partial x''}\frac{\Delta v^{32}(x' - x'') - \Delta v^{12}(x''' - x'')}{\Delta v^{32}\,\Delta\eta^{12} - \Delta v^{12}\,\Delta\eta^{32}}. \quad (14)$$

This is a general equation which applies to any three-phase equilibrium in a two-component system.

The terms of the form $\left[v' - v'' - (x' - x'')\frac{\partial v''}{\partial x''}\right]$ require some discussion. In equation (6) [129] the volume and entropy terms represent difference in specific volume and specific entropy, and, taken as a whole, represent the volume and entropy changes taking place along the three-phase curve. Equation (12) refers to two phases in a two-component system, and hence to a divariant equilibrium. The coefficients of dp and dt in this case refer to the volume and entropy changes which take place when one gram of the first phase separates from a large quantity of the second, a type of change called "differential," "partial," or "fictive."

14. Correlation of the t-x and p-t Curves. Consider the application of equation (14) to the t-x curve of KNO_3 in the binary system, H_2O-KNO_3, and let the phases with single, double, and triple accents be vapor, liquid (saturated solution), and solid, respectively. The equation then becomes

$$\frac{dt}{dx''} = -\frac{1}{1 - x''}\frac{\partial \mu_2}{\partial x''}\frac{\Delta v^{sl}(x^v - x^l) - \Delta v^{vl}(x^s - x^l)}{\Delta v^{sl}\,\Delta\eta^{vl} - \Delta v^{vl}\,\Delta\eta^{sl}}.$$

The terms $\frac{1}{1 - x''}$ and $\frac{\partial \mu_2}{\partial x''}$ are necessarily positive. In the denominator, Δv^{sl} is usually negative, $\Delta\eta^{vl}$ always positive, hence the first term is usually negative. In the second term,

Δv^{vl} is positive, $\Delta \eta^{sl}$ negative, making the second term always negative. Because of the preponderance of Δv^{vl} the second term is greater than the first and, as this term has a negative sign, the denominator is always positive. In the numerator, Δv^{sl} is usually negative and $(x^v - x^l)$ negative, so the first term is positive in the usual case. The quantity Δv^{vl} is dominant in the numerator also; its product with the term $(x^s - x^l)$ is always positive, but as it bears a negative sign, the numerator is usually negative. This makes $\frac{dt}{dx''}$ positive, and the *t-x* curve has a positive slope. When, however, the composition of the solution has become very close to that of the solid, the negative second term becomes equal to the positive first term, and the *t-x* curve has a horizontal tangent, followed by a negative slope. In such cases as H_2O-KNO_3 this detail of the solubility curve is not detectable experimentally, but that it is necessarily present follows from the correlation with the *p-t* curve. The *p-t* curve passes first through a point of maximum pressure, then one of maximum temperature, and at its end-point coincides with the melting-point curve of KNO_3, the univariant equilibrium (solid + liquid) in the unary system, KNO_3.

15. Equilibrium Involving Solid Solutions. It was mentioned above that solid KNO_3 exists in two enantiotropic modifications, but that consideration of this was not pertinent to the discussion. The two forms are both pure KNO_3, there is no solid solution, and the inversion point extends across the diagram at constant temperature. It will, however, cause an abrupt change in slope on both the *t-x* and *p-t* curves of the equilibrium, vapor + liquid + solid. In the not unusual case in other systems in which one or both of two enantiotropic forms takes into solid solution some of the other component, the equilibrium becomes univariant, and the inversion temperature is either raised or lowered, depending on which of the two forms contains the greater quantity of the other component. It will be interesting to apply equation (14) to this case.

Let the phases with single, double, and triple accents be vapor, the high-temperature (α) form, and the low-temperature (β) form. The equation becomes

$$\frac{dt}{dx''} = -\frac{1}{1-x''}\frac{\partial \mu_2}{\partial x''}\frac{\Delta v^{\beta\alpha}\,(x^{v} - x^{\alpha}) - \Delta v^{v\alpha}\,(x^{\beta} - x^{\alpha})}{\Delta v^{\beta\alpha}\,\Delta \eta^{v\alpha} - \Delta v^{v\alpha}\,\Delta \eta^{\beta\alpha}}.$$

As before, $\frac{1}{1 - x''}$ and $\frac{\partial \mu_2}{\partial x''}$ are necessarily positive. In the denominator, $\Delta v^{\beta\alpha}$ is small and may be either positive or negative; $\Delta \eta^{v\alpha}$ is positive. In the second term, $\Delta v^{v\alpha}$ is large and positive; $\Delta \eta^{\beta\alpha}$ negative, since by hypothesis the α-form is the high-temperature phase, and hence has greater entropy. The product is negative; because of the large numerical value of the term $\Delta v^{v\alpha}$, the second term in the denominator predominates, and, being affected by a negative sign, the resultant denominator is always positive. In the numerator the first term is of uncertain sign, but is smaller than the second term. The second term is the dominant one; $\Delta v^{v\alpha}$ is large and positive, and the sign of the numerator, and hence of the entire expression, is determined by, and is the same as, that of the composition difference $(x^{\beta} - x^{\alpha})$. When the high-temperature, or α-form, takes more of the other component into solid solution, $(x^{\beta} - x^{\alpha})$ is positive, $\frac{dt}{dx''}$ is positive, and the inversion temperature is lowered by solid solution. When the low temperature, or β-form, takes the greater quantity of the other component into solid solution, the inversion temperature is raised. A well-known example of the second case is the raising of the inversion temperature of the low-temperature form of $CaO \cdot SiO_2$, wollastonite, by solid solution of $MgO \cdot SiO_2$.

The further treatment of equilibria in which there is solid solution is a simple extension of the above methods. The composition of the solid phase is no longer constant, but variable, a circumstance for which allowance is readily made in the discussion. In addition, the entropy and volume are no longer independent of the composition, but this again rarely leads to complications. In the case of solid solution in systems in which both components are volatile all of the coexisting phases in a univariant equilibrium may be of variable composition, but since compositions come into the equations as differences the detailed application of the equations above presents no difficulty.

16. Application of Equation [97] to a System in Which Compounds Are Formed. H_2O-$CaCl_2$. We have considered the application of equation (8) to the simplest type of system, that in which there is but one phase of variable composition, and no compounds are formed. It will be of interest to see what additional complications are introduced by the formation of compounds, and as illustration the system, H_2O-$CaCl_2$, will be chosen. Projections of the solid pressure-temperature-composition model are shown in Fig. 3.*

The invariant point, ice + $CaCl_2 \cdot 6H_2O$ + solution + vapor, is at $-55°$, and the pressure is but a fraction of a millimeter. The compound, $CaCl_2 \cdot 6H_2O$, contains 50.66 per cent $CaCl_2$, and the cryohydrate solution, 29.8 per cent. The equation of the pressure-temperature curve of the solutions saturated with $CaCl_2 \cdot 6H_2O$ is

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) + \dfrac{x^l}{0.5066 - x^l}(\eta^s - \eta^l)}{(v^v - v^l) + \dfrac{x^l}{0.5066 - x^l}(v^s - v^l)}.$$

As in the preceding case the volume change of the water vapor is the dominating factor at low temperatures, causing the curve to be concave upward (Fig. 3). As the temperature is raised the fractional coefficient of the second term becomes of increasing importance, as before, and again a point of inflection of the *p-t* curve is reached at 18°; the solution at this temperature contains 42 per cent $CaCl_2$, so the coefficient of the second term is now 0.42/(0.5066–0.42), or about 4.2. The curvature falls off rapidly with increase in the $CaCl_2$ content, and becomes zero at 28° and 48.5 per cent $CaCl_2$. Since at this point

$$\frac{x^l}{0.5066 - x^l} = \frac{\eta^v - \eta^l}{\eta^s - \eta^l},$$

the ratio of the entropy of vaporization to the entropy of solution is 0.485/(0.506 − 0.885), or about 23 to 1. With further increase in the $CaCl_2$ content the slope of the *p-t* curve becomes negative, and the pressure falls with increasing temperature.

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* H. W. Bakhuis Roozeboom, *Z. physik. Chem.*, **4**, 31 (1889).

17. The Minimum Melting Point of a Dissociating Compound. It will be remembered that in the discussion of the system, H_2O-KNO_3, it was stated that when the liquid phase was very close in composition to the solid phase, the coefficient of the second term would become large enough for the small negative volume difference (solid − liquid), multiplied by the large coefficient, to equal the very much larger and positive volume difference (vapor − liquid), but that the effect would be difficult to detect in such a system. When that is the case, the denominator approaches zero, the slope* of the *p-t* curve, *dp/dt*, becomes infinite, the curve has a vertical tangent, and hence a point of maximum temperature. This is shown clearly in this system. On further increase in the $CaCl_2$ content of the solution, a maximum temperature is found, after which both temperature and pressure fall. Two effects take place very close together here; first, the liquid approaches the solid so closely that the denominator becomes zero, then the two compositions become identical. When the two phases, solid and liquid, have the same composition, the equation of the *p-t* curve becomes

$$\frac{dp}{dt} = \frac{\eta^s - \eta^l}{v^s - v^l},$$

which is the equation of the melting-point curve of the hexahydrate. The condensed system, liquid $CaCl_2 \cdot 6H_2O$ + solid $CaCl_2 \cdot 6H_2O$, is one of the great majority of cases where melting causes expansion; both the specific entropy and the specific volume of the liquid are greater than those of the solid phase. This melting point of the hydrate is called the "minimum melting point" because it is the lowest temperature at which solid and liquid of the same composition can exist together in equilibrium; a whole series of such melting points can be obtained at higher pressures in the absence of vapor along the melting-point curve of the hydrate, the curve of the condensed system, liquid-solid. It should be pointed out that this minimum melting point is not at the point of maximum temperature, but at a lower temperature. The point of maximum temperature is found at such a salt content that the denominator becomes zero, as previously stated, while the minimum melting point lies at a slightly higher salt content, and a lower temperature and pressure. In a system containing a volatile component the point of maximum temperature is not at the composition of the compound, as is the case in systems of non-volatile components or in condensed systems, but at a composition slightly displaced toward the volatile component. In the case of $CaCl_2 \cdot 6H_2O$ the difference is very small, and the two points have never been separated, but at higher temperatures and pressures the difference is no longer negligible.

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* Cf. footnote on page 251; t is represented by the axis of x, p by the axis of y, hence $\frac{dy}{dx}$ is equivalent to $\frac{dp}{dt}$.

After the minimum melting point has been passed, the coefficient of the second term in the denominator becomes negative, so that in both numerator and denominator the second term, the entropy and volume differences (solid-liquid), in themselves negative, are multiplied by a negative coefficient, hence the second term in both becomes positive, and is to be added to the positive first terms. The slope of the *p-t* curve is then positive, and remains so until the invariant point, $CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O$ + solution + vapor, is reached, at which a new solid phase, calcium chloride tetrahydrate, makes its appearance. The *p-t* curves that proceed from this invariant point when different phases disappear present some novel features, and are considered in detail below.

18. Correlation of the t-x and p-t Curves. The sequence of the points of maximum temperature and minimum melting point on the three-phase curve, vapor + liquid (saturated solution) + $CaCl_2 \cdot 6H_2O$, is brought out especially well by the application of equation (14), which in this case becomes

$$\frac{dt}{dx^l} = -\frac{1}{1 - x^l}\frac{d\mu_1}{dx^l}\frac{\Delta v^{sl}(0 - x^l) - \Delta v^{vl}(0.5066 - x^l)}{\Delta v^{sl}\,\Delta\eta^{vl} - \Delta v^{vl}\,\Delta\eta^{sl}}$$

As before, the denominator is positive, and the sign of the numerator is determined by the sign of $(x^s - x^l) = (0.5066 - x^l)$. When the difference $(x^s - x^l)$ is large and positive, the second term predominates, the numerator is negative, and dt/dx^l is positive; as $(x^s - x^l)$ approaches zero, the numerator first approaches zero, and both the *p-t* and *t-x* curves show a point of maximum temperature. The numerator remains positive when $x^s = x^l$, at the minimum melting point, which is no special point on the *t-x* curve except when dealing with condensed systems, in which the vapor phase is absent. In the case in which Δv^{sl} is positive, the numerator is still negative, hence dt/dx^l still positive, when $x^s = x^l$, and at the point of maximum temperature $x^s < x^l$. In systems in which both components are volatile, complications arise from the varying composition of the vapor phase, and interesting special cases arise when the vapor-pressure curve of the liquid shows either maximum or minimum points, and also in connection with the location of the maximum sublimation temperature, especially with dissociating compounds.*

19. The Equilibrium between a Dissociating Hydrate and Its Products of Dissociation. From the invariant point, $CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O$ + solution + vapor (Fig. 3), four univariant equilibria are obtained by the disappearance of each, separately, of these four phases. If the liquid phase disappears we have the three phases, hexahydrate, tetrahydrate, and vapor; since all of these phases are of constant composition the pressure is a function of the temperature only; there is no concomitant change in composition of one of the phases. Our equation becomes

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^t) - \dfrac{x^v - x^t}{x^h - x^t}(\eta^h - \eta^t)}{(v^v - v^t) - \dfrac{x^v - x^t}{x^h - x^t}(v^h - v^t)},$$

in which the superscripts *h* and *t* represent the hexahydrate and the tetrahydrate, respectively. Substituting the numerical values of x^v, $x^{\text{tetrahydrate}}$ and $x^{\text{hexahydrate}}$, 0, 0.6063, and 0.5066, respectively, gives the value of 6.06 as the constant coefficient of the second term. The equation now becomes

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* J. D. van der Waals, *Verslag. Akad. Wetenschappen Amsterdam*, **5**, 482 (1897). A. Smits, *Z. physik. Chem.*, **54**, 5 (1906).

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^t) - 6.06\,(\eta^h - \eta^t)}{(v^v - v^t) - 6.06\,(v^h - v^t)}.$$

The numerator of this is always positive. The entropy difference (vapor − tetrahydrate) is always positive. The entropy difference (hexahydrate − tetrahydrate) is negative, since the decomposition of hexahydrate into tetrahydrate and solution, to be considered later, absorbs heat, and this negative term is multiplied by a negative coefficient, making the second term positive. The denominator is large and positive, because of the very large specific volume of the vapor. The value of dp/dt is consequently positive, and the pressure increases with the temperature, as is the case with the dissociation pressure of the hexahydrate. It is to be observed that this equilib-

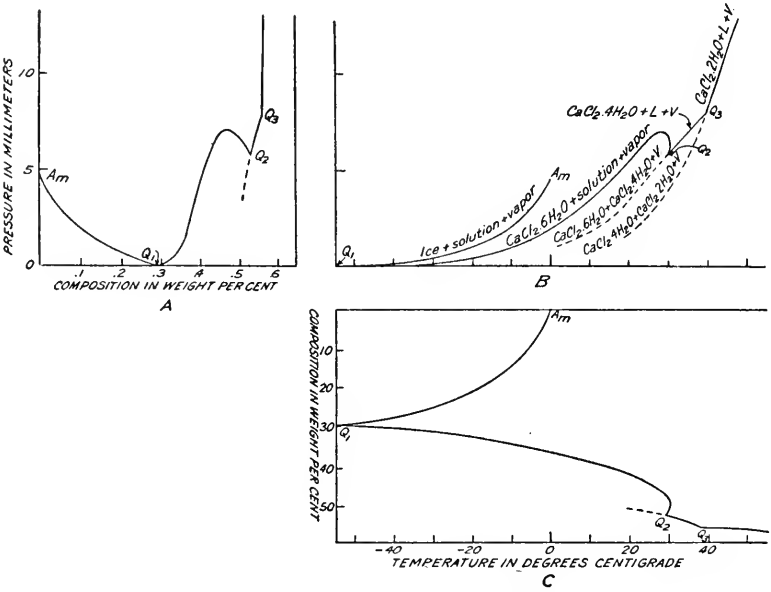

FIG. 3. The binary system, H_2O-$CaCl_2$. Diagrams A, B, and C are the projections of the curves representing univariant equilibria in the solid p-t-x model on the p-x, p-t, and t-x planes, respectively.

rium requires the presence of both solid phases, calcium chloride hexahydrate and calcium chloride tetrahydrate, which, together with the vapor, make three phases, hence three equations. The common name, dissociation-pressure curve of the hexahydrate, is misleading; it is the univariant equilibrium involving all three phases. The invariant point is the high temperature termination of the stable portion of this curve; when a mixture of these two solids, together with vapor, is heated, at the invariant point some solution is formed; some of the solid melts to form the eutectic liquid.

20. The Equilibrium, Two Solids + Liquid. A second univariant equilibrium is that formed by the disappearance of vapor. This is the condensed system composed of the two hydrates and the eutectic liquid; the composition of the eutectic liquid and the eutectic temperature both change as the pressure is increased, but the change is small, and will not be considered further.

21. The Equilibrium, Solid + Solution + Vapor. Two univariant equilibria between solid, liquid, and vapor can be formed, the solubility curves of the hexahydrate and the tetrahydrate. The first of these, the equilibrium vapor + solution + $CaCl_2 \cdot 6H_2O$, has already been considered; both temperature and pressure increase from the invariant point with increase in water content of the solution. At the minimum melting point solid hexahydrate melts to form a liquid of the same composition; this is called a congruent melting point.

The other equilibrium between solid, liquid, and vapor is the solubility curve of the tetrahydrate. Application of equation (8) to this brings out no novel features; temperature and pressure both increase as the solution becomes richer in $CaCl_2$, and this portion of the *p-t* curve is concave downward over its entire course. It differs from the preceding, however, because of the circumstance that, before the point at which the *p-t* curve has a horizontal tangent, a new solid phase appears, calcium chloride dihydrate. This gives rise to another invariant point, at which the four phases are tetrahydrate, dihydrate, solution, and vapor. In the case of the hexahydrate the invariant solution was richer in $CaCl_2$ than the compound disappearing, the solution was a eutectic, and the compound had a congruent melting point. The solution at this invariant point contains 56.4 per cent $CaCl_2$, while the tetrahydrate contains 60.6 per cent $CaCl_2$; substitution of these values in equation (8) gives

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) + \dfrac{0.564}{0.606 - 0.564}(\eta^s - \eta^l)}{(v^v - v^l) + 13.4\,(v^s - v^l)}.$$

The positive entropy of vaporization is larger than the negative entropy of fusion multiplied by its coefficient, dp/dt is still positive, and both temperature and pressure are increasing along the solubility curve of the tetrahydrate at the invariant point. This solubility curve differs from the preceding in that solid and liquid do not have the same composition at any point; calcium chloride tetrahydrate has an incongruent melting point and the invariant point is not a eutectic but a transition point. Pure hexahydrate, when heated, melts to form a liquid of its own composition; pure tetrahydrate decomposes into dihydrate and saturated solution of the composition of the solution at the invariant point.

From this invariant point three other univariant equilibria can be obtained. One of them is the condensed system, whose *p-t* curve is almost vertical; a second is the dissociation-pressure curve of the tetrahydrate, the univariant equilibrium, tetrahydrate + dihydrate + vapor; the third is the solubility curve of the dihydrate. The curves representing these equilibria are shown in Fig. 3.

22. Types of Invariant Points and Univariant Systems. While the preceding discussion has dealt primarily with the application of the Phase Rule to simple systems having only one phase of variable composition, with especial reference to the direct application of equation (1) [97], the modifications necessary to include additional phases of variable composition have been indicated. In a binary system, coexistence of three phases constitutes a univariant system, of four phases, an invariant system, and the possible types of such equilibria are the possible permutations of solid, liquid, and vapor, with the additional empirical restrictions that there can be but one vapor phase, and, in a binary system, but two liquid phases. The possible types, representing vapor, liquid, and solid by V, L, and S, are as follows:

TYPES OF INVARIANT POINTS; FOUR COEXISTING PHASES

No.	Solid	Liquid	Vapor
1	$S_1S_2S_3S_4$	—	—
2	$S_1S_2S_3$	L	—
3	$S_1S_2S_3$	—	V
4	S_1S_2	L_1L_2	—
5	S_1S_2	L	V
6	S	L_1L_2	V

TYPES OF UNIVARIANT SYSTEMS; THREE COEXISTING PHASES, AND THE INVARIANT TYPES FROM WHICH THEY MAY BE DERIVED

				Derived from
1	$S_1S_2S_3$	—	—	1,2,3
2	S_1S_2	L	—	2,4,5
3	S_1S_2	—	V	3,5
4	S	L_1L_2	—	4,6
5	S	L	V	5,6
6	—	L_1L_2	V	6

In these various types of univariant systems, one, two, or three of the phases may be of variable composition. Type 1, $S_1S_2S_3$, is only of interest where there is solid solution. Type 2, S_1S_2L, is the "condensed" equilibrium, giving the change with pressure of the temperature and composition of a eutectic or an incongruent melting point. The most common example of type 3 is the "dissociation pressure" curve of a salt hydrate; and of type 5, the solubility curve of a salt in water, or the melting-point curve of a fused salt or metal system. Examples of all of the types have been discussed, except those containing two liquid layers, types 4 and 6. Systems in which two liquid layers are formed are of both theoretical and practical interest, and water-phenol is an excellent example.

23. Equilibrium Involving Two Immiscible Liquids. Water-phenol. In the discussion of the system, water-phenol,* the compound formed between the two components will not be considered. It is not readily formed; metastable equilibria between phenol and water in which it is not formed are more easily realized than the stable ones, with formation of the compound; and its consideration would involve no new principles. On addition of phenol to water, the ice curve is first traced, down to the eutectic between ice and phenol crystals. The invariant point at which both ice and phenol can coexist,

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* F. H. Rhodes and A. L. Markley, *J. Phys. Chem.*, **25**, 527 (1921).

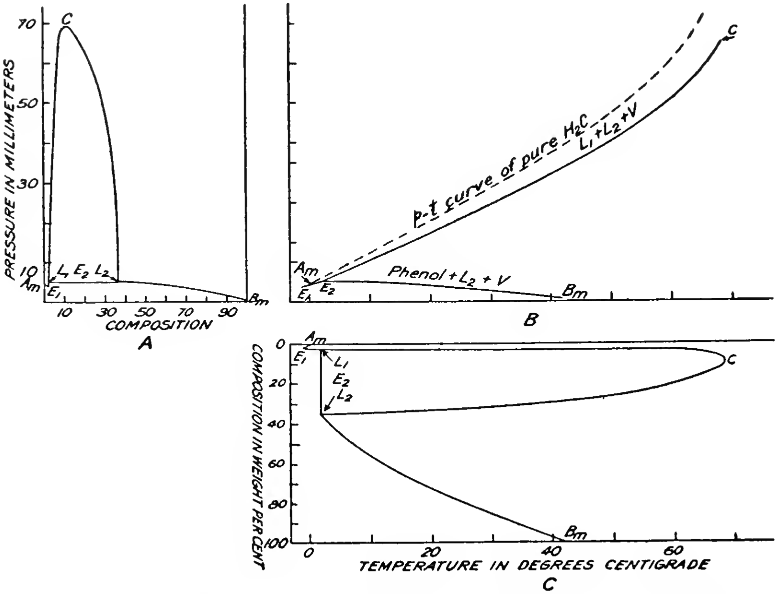

FIG. 4. The binary system, H_2O-phenol. Diagrams *A*, *B*, and *C* are the projections of the curves representing univariant equilibria in the solid *p-t-x* model on the *p-x*, *p-t*, and *t-x* planes, respectively.

together with solution and vapor, is at −1.2° (Fig. 4) and at a concentration of phenol of less than one per cent. As the temperature is raised above this point, the solubility of phenol increases slightly, until at 1.7° the saturated solution contains about 1.8 per cent phenol. At this temperature the solid phenol in equilibrium with the solution melts, taking up water, and forming a second liquid layer. We have then four phases, solid phenol, a liquid containing 1.8 per cent phenol, a second liquid immiscible with the first and containing about 36 per cent of phenol, and a vapor phase containing so small an amount of phenol that we may consider it as pure water. Four univariant equilibria proceed from this invariant point. The equilibrium, solid phenol + solution + vapor, the solubility curve of solid phenol; and the equilibrium, solid phenol + two liquids, a condensed system giving the change with pressure in the composition of the two layers in equilibrium with solid; present no new features, and will not be considered. The equilibrium between vapor, the water-rich liquid, and the phenol-rich liquid is of greater interest. At the invariant point equation (8) becomes

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^{l_1}) - \dfrac{x^v - x^{l_1}}{x^{l_2} - x^{l_1}}(\eta^{l_2} - \eta^{l_1})}{(v^v - v^{l_1}) - \dfrac{x^v - x^{l_1}}{x^{l_2} - x^{l_1}}(v^{l_2} - v^{l_1})}.$$

Substituting the values 0, 0.018 and 0.36 for the composition of the vapor, the water-rich liquid and the phenol-rich liquid, respectively, gives us

$$\frac{dp}{dt} = \frac{(\eta^v - \eta^l) - \dfrac{0.018}{0.36 - 0.018}(\eta^{l_2} - \eta^{l_1})}{(v^v - v^l) - 0.053\,(v^{l_2} - v^{l_1})},$$

and in this case also the entropy and volume of the water are the dominating factors. The *p-t* curve accordingly is concave upward. As the temperature is increased, the two liquids approach each other in composition, the water-rich layer changing less than the phenol-rich layer. But at the same time their specific entropies and specific volumes approach each other, since both are liquids composed of the same components and increasingly close to each other in composition. For this reason the increasing value of the coefficient of the second term is offset by the decrease in the second term itself, and no maximum pressure is found. Finally, the two phases become identical in composition and properties. At the same time that the difference in composition becomes zero the difference in entropy and the difference in volume become zero, and the equation becomes indeterminate. This is as should be expected; the three-phase system was univariant because there were three equations between the three quantities, pressure, temperature, and composition. When the two liquid phases become identical, not only in composition but also in properties, there are no longer three phases, but two only, and the system is no longer univariant but divariant. In the case of calcium chloride hexahydrate, when the liquid and solid phases had the same composition at the minimum melting point, there was still an entropy difference, since it takes heat to melt a solid, and a volume difference. At the temperature at which the two liquids merge into one another, all distinctions between the phases disappear, and there are but two phases, liquid and vapor. At this temperature there may be not only the critical solution, but also any other mixture of liquid phenol and water; the composition of the solution or the vapor pressure must be fixed in order to completely determine the system.

The critical liquid itself is, however, completely determined. At a temperature very near to the critical solution temperature of the mixture, there are still three equations, and the critical solution is determined by the additional condition that the two phases become identical. We have, then, four equations; three of the type of (1) [97], and the additional equation expressing the condition of identity between the two liquids, so this solution is uniquely determined.

If from the invariant point, solid phenol + two liquids + vapor, the water-rich layer disappears, we have the univariant equilibrium, solid phenol + a phenol-rich liquid + vapor. This equilibrium will be realized if the total phenol content of the mixture be greater than that of the phenol-rich liquid, and constitutes another branch of the solubility curve of phenol in water, or of the melting-point curve of phenol-water mixtures along which the solubility of phenol in water increases uniformly, until the melting point of phenol is reached. This curve does not differ in any important respect from the upper portion of the H_2O-KNO_3 curve, except that the melting point of phenol is so much lower than that of KNO_3 that the vapor pressure of the solutions probably decreases, without first rising to a maximum.

V. Application of Equation [97] to Systems of Three Components

24. Transformation and Interpretation of Equations. Problems involving a greater number of components may be solved by the same analytical method of treatment, but it will not be possible to elaborate the discussion for systems of more than three components, or to give a complete treatment of ternary systems. *When equation (6) [129] is applied to a three-component system it becomes

$$\frac{dp}{dt} = \frac{\begin{vmatrix} H' & m_1' & m_2' & m_3' \\ H'' & m_1'' & m_2'' & m_3'' \\ H''' & m_1''' & m_2''' & m_3''' \\ H^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} V' & m_1' & m_2' & m_3' \\ V'' & m_1'' & m_2'' & m_3'' \\ V''' & m_1''' & m_2''' & m_3''' \\ V^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}},$$

in which the composition of the phases is represented by the actual masses of the components, m_1, m_2, and m_3, and the volume and entropy refer to the total mass. By setting $m_1 + m_2 + m_3 = 1$, $x = m_2/(m_1 + m_2 + m_3)$, $y = m_3/(m_1 + m_2 + m_3)$, we get†

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* From this point to the end of section (28), and again from (30), third paragraph (p. 281), to the bottom of p. 291, the text is taken, with some omissions, alterations and additions, from the article of G. W. Morey and E. D. Williamson, *Jour. Am. Chem. Soc.*, **40**, 59–84 (1917).

† This equation has been used in the form of a determinant because of the great convenience of that form of notation. For those not familiar with determinants it may be said that this constitutes a shorthand method of indicating the familiar operation of elimination by cross multiplication. When dealing with systems of more than three components such a notation becomes almost indispensable.

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \eta' & 1 & x' & y' \\ \eta'' & 1 & x'' & y'' \\ \eta''' & 1 & x''' & y''' \\ \eta^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}}{\begin{vmatrix} v' & 1 & x' & y' \\ v'' & 1 & x'' & y'' \\ v''' & 1 & x''' & y''' \\ v^{IV} & 1 & x^{IV} & y^{IV} \end{vmatrix}},$$

in which composition is represented by the weight fractions x, y, and $1 - x - y$ of the three components. Expansion of the right-hand side of this equation gives

$$\frac{\eta' \begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - \eta'' \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \eta''' \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - \eta^{IV} \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}}{v' \begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - v'' \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + v''' \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} - v^{IV} \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}} \quad (15)$$

The coefficients of η', η'', v', v'', etc., represent the areas of the triangles $P''P'''P^{IV}$, $P'P'''P^{IV}$, $P'P''P^{IV}$, and $P'P''P'''$, respectively. It is important to bear in mind the direction in which a given triangle is circumscribed, since, if the area of the triangle $P'P''P'''$ is positive, that of the triangle $P''P'P'''$ is negative.

Since the above coefficients represent areas, we will denote the determinants by the letter A, followed by subscripts indicating which triangle is meant, and the direction in which it is circumscribed is given by the order of the subscripts. Thus A_{123} represents the determinant

$$\begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix},$$

the area of the triangle $P'P''P'''$. The equation becomes

$$\frac{dp}{dt} = \frac{A_{234}\,\eta' - A_{134}\,\eta'' + A_{124}\,\eta''' - A_{123}\,\eta^{IV}}{A_{234}\,v' - A_{134}\,v'' + A_{124}\,v''' - A_{123}\,v^{IV}}.$$

It is easy to show that

$$\begin{vmatrix} 1 & x'' & y'' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} = \begin{vmatrix} 1 & x' & y' \\ 1 & x''' & y''' \\ 1 & x^{IV} & y^{IV} \end{vmatrix} + \begin{vmatrix} 1 & x' & y' \\ 1 & x'' & y'' \\ 1 & x''' & y''' \end{vmatrix}$$

or, expressed in areas, that

$$A_{234} + A_{124} = A_{134} + A_{123}.$$

Hence we can eliminate any one of the above coefficients,* and cast the equation into the form

$$\frac{dp}{dt} = \frac{(\eta''' - \eta^{IV}) + \frac{A_{234}}{A_{123}}(\eta' - \eta''') - \frac{A_{134}}{A_{123}}(\eta'' - \eta''')}{(v''' - v^{IV}) + \frac{A_{234}}{A_{123}}(v' - v''') - \frac{A_{134}}{A_{123}}(v'' - v''')}. \quad (16)$$

25. Equilibrium, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ + Solution + Vapor. A systematic application of this equation to the numerous types of equilibria that may arise in ternary systems will not be possible, and the discussion will be confined to one system, the ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2,† which contains examples of several common types of univariant equilibria. The experimental details are given in the first of the papers just cited; the phase relationships are shown in Figs. 5 to 8. Figure 5 shows the isothermal polybaric saturation curves; Fig. 6, the boundary curves and invariant points;‡ Fig. 7, the experimentally determined pressure-temperature curves; and Fig. 8, a diagrammatic representation of the same curves. When equation (16) is applied to the ternary equilibrium $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ +

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* In a 2-component system the corresponding determinant coefficients represent the lengths of lines; in a 4-component system, volumes of solids; in an n-component system, the supervolumes of n-dimensional supersolids.

† G. W. Morey and C. N. Fenner, *J. Am. Chem. Soc.*, **39**, 1173 (1917). G. W. Morey and E. D. Williamson, *J. Am. Chem. Soc.*, **40**, 59 (1918). F. C. Kracek, N. L. Bowen and G. W. Morey, *J. Phys. Chem.*, **33**, 1857 (1929).

‡ In the original, a eutectic between $K_2O \cdot 2SiO_2$ and SiO_2 is indicated, but later studies (Kracek, Bowen and Morey, op. cit.) have shown that $K_2O \cdot 4SiO_2$ is formed, and the compound, $K_2O \cdot 4SiO_2 \cdot H_2O$, may be considered as a hydrate of the former. The necessary changes in the diagrams have been made.

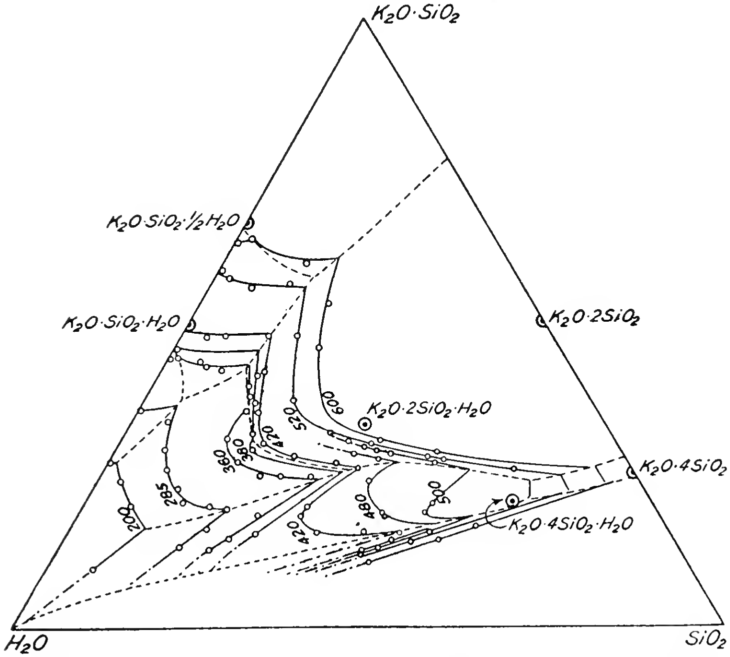

Fig. 5. The ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2. The full lines are the isothermal polybaric saturation curves at the temperatures indicated. The broken curves are the boundary curves between the various fields.

$K_2O \cdot 2SiO_2$ + L + V (curve 6*c*, Figs. 5–8), the curve which proceeds from the quintuple point Q_2 to quintuple point Q_1, it becomes

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \dfrac{A_{2lv}}{A_{12l}}(\eta' - \eta^l) - \dfrac{A_{1lv}}{A_{12l}}(\eta'' - \eta^l)}{(v^l - v^v) + \dfrac{A_{2lv}}{A_{12l}}(v' - v^l) - \dfrac{A_{1lv}}{A_{12l}}(v'' - v^l)},$$

in which S′ and S″ represent the compounds $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ and $K_2O \cdot 2SiO_2 \cdot$ At Q_2, the terms $(\eta^l - \eta^v)$ and $(v^l - v^v)$, both of which are negative and much larger than the other terms, preponderate; *dp*/*dt* is positive. As with increasing tem-

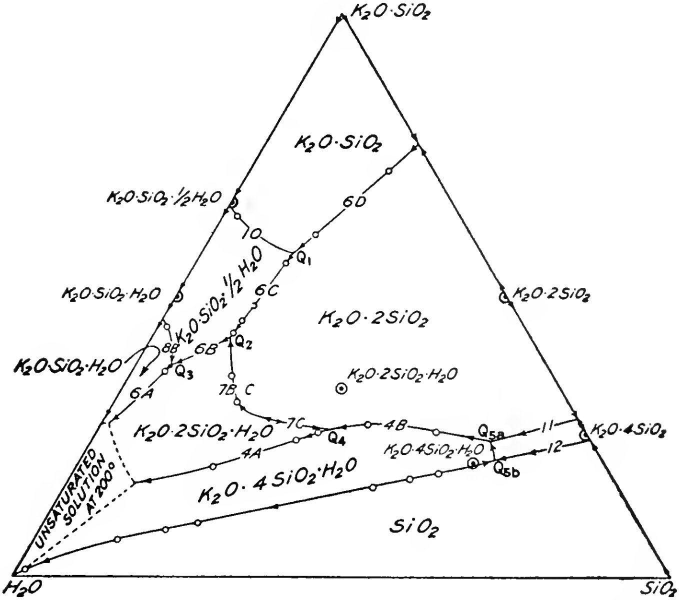
K₂O·SiO₂
K₂O·SiO₂
K₂O·SiO₂·½H₂O
6D
10
Q₁
K₂O·SiO₂·½H₂O
6C
K₂O·2SiO₂
K₂O·2SiO₂
K₂O·SiO₂·H₂O
K₂O·SiO₂·H₂O
8B
6B
Q₂
Q₃
6A
7B
C
K₂O·2SiO₂·H₂O
K₂O·2SiO₂·H₂O
7C
Q₄
4B
Q5a
11
K₂O·4SiO₂
4A
K₂O·4SiO₂·H₂O
12
Q5b
K₂O·4SiO₂·H₂O
UNSATURATED SOLUTION AT 200°
SiO₂
H₂O
SiO₂

FIG. 6. The ternary system, H_2O-$K_2O\cdot SiO_2$-SiO_2. This diagram shows the various boundary curves, which give the locus of the composition of the liquid phase in the various univariant equilibria. The invariant (quintuple) points are designated by the letter Q; the numbers on the curves are the same in Figs. 6, 7, and 8. Following is a list of phases stable along each curve.

Curve 2. $V + L + K_2O\cdot 4SiO_2\cdot H_2O + SiO_2$
Curve 4a. $V + L + K_2O\cdot 2SiO_2\cdot H_2O + K_2O\cdot 4SiO_2\cdot H_2O$
Curve 4b. $V + L + K_2O\cdot 2SiO_2 + K_2O\cdot 4SiO_2\cdot H_2O$
Curve 6a. $V + L + K_2O\cdot SiO_2\cdot H_2O + K_2O\cdot 2SiO_2\cdot H_2O$
Curve 6b. $V + L + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot 2SiO_2\cdot H_2O$
Curve 6c. $V + L + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot 2SiO_2$
Curve 6d. $V + L + K_2O\cdot SiO_2 + K_2O\cdot 2SiO_2$
Curve 7a. $V + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot 2SiO_2\cdot H_2O + K_2O\cdot 2SiO_2$
Curve 7a + 7b. $V + L + K_2O\cdot 2SiO_2\cdot H_2O + K_2O\cdot 2SiO_2 + K_2O\cdot 4SiO_2\cdot H_2O$
Curve 7b + 7c. $V + L + K_2O\cdot 2SiO_2\cdot H_2O + K_2O\cdot 2SiO_2$
Curve 7a + 7b + 7c. $V + K_2O\cdot 2SiO_2\cdot H_2O + K_2O\cdot 2SiO_2$, in binary system, H_2O-$K_2O\cdot 2SiO_2$
Curve 8a. $V + K_2O\cdot SiO_2\cdot H_2O + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot 2SiO_2\cdot H_2O$
Curve 8b. $V + L + K_2O\cdot SiO_2\cdot H_2O + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O$
Curve 8a + 8b. $V + K_2O\cdot SiO_2\cdot H_2O + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O$, in binary system, H_2O-$K_2O\cdot SiO_2$
Curve 9. $V + K_2O\cdot 4SiO_2\cdot H_2O + K_2O\cdot 4SiO_2 + SiO_2$
Curve 10a. $V + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot SiO_2 + K_2O\cdot 2SiO_2$
Curve 10b. $V + L + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot SiO_2$
Curve 10a + 10b. $V + K_2O\cdot SiO_2\cdot \frac{1}{2}H_2O + K_2O\cdot SiO_2$, in binary system, H_2O-$K_2O\cdot SiO_2$
Curve 11. $V + L + K_2O\cdot 2SiO_2 + K_2O\cdot 4SiO_2$
Curve 12. $V + L + K_2O\cdot 4SiO_2 + SiO_2$

perature the liquid traces the curve Q_2Q_1, the triangle A_{12l} becomes smaller, while the triangles A_{2lv} and A_{1lv} become larger. The values of the coefficients of $(\eta' - \eta^l)$ and $(\eta'' - \eta^l)$ in the numerator and $(v' - v^l)$ and $(v'' - v^l)$ in the denominator thus increase rapidly. Since the value of $(v^l - v^v)$ is comparatively large, this increase in the coefficients at first affects materially

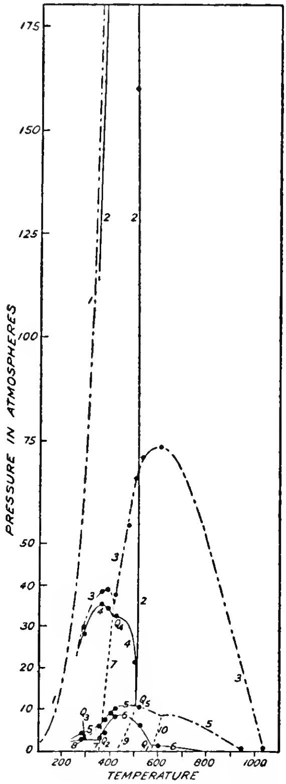

FIG. 7. The ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2. This diagram shows the experimentally determined p-t curves for the various univariant equilibria. The dot-dash curves represent univariant equilibria in the binary systems, H_2O-$K_2O \cdot SiO_2$ and H_2O-$K_2O \cdot 2SiO_2$; the full curves the ternary univariant equilibria, V + L + 2 solids; the dotted curves the ternary univariant equilibria, V + 3 solids. The invariant points Q_{5a} and Q_{5b} are shown as point Q_5, and the curves 11 and 12 are not shown.

the value of the numerator only. As the liquid follows the curve Q_2Q_1 the value of the last two terms of the numerator soon becomes equal to the value of the first term. The numerator then becomes zero, dp/dt becomes zero, and the curve has a horizontal* tangent. It will be observed that such a point of maximum pressure is found on many of the p-t curves

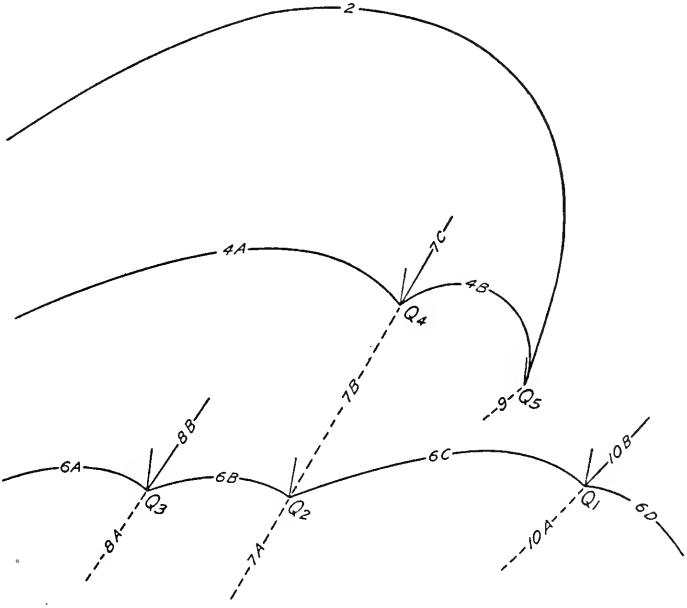

FIG. 8. The ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2. A diagrammatic representation of the p-t curves shown in Fig. 7; the numbers on the curves are the same in Figs. 6, 7, and 8. The invariant points Q_{5a} and Q_{5b} are shown as point Q_5, and the curves 11 and 12 are not shown.

representing univariant equilibrium between two solids, liquid and vapor in the system. It is most pronounced in the univariant equilibrium, $K_2O \cdot 4SiO_2 \cdot H_2O + SiO_2 + L + V$.

On further increase in temperature the numerator becomes positive, the denominator remains negative, hence dp/dt is negative. This continues until, in the case we are considering, the phase $K_2O \cdot SiO_2$ makes its appearance at the quintuple point Q_1. Consider the metastable continuation of the curve, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L + V$ (curve 6*c*).

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* Cf. footnote, page 257; $\frac{dp}{dt}$ takes the place of $\frac{dy}{dx}$ of analytical geometry.

Beyond Q_1, on further increase in temperature the triangle A_{12l} approaches zero, the coefficients of $(v' - v^l)$ and $(v'' - v^l)$ in the denominator increase rapidly, reaching such a value that the sum of the last two terms in the denominator becomes numerically equal to the first, in spite of the large value of $(v^l - v^v)$. The denominator then approaches zero, and dp/dt becomes infinite. At this point the *p-t* curve has a vertical tangent. Beyond this point dp/dt again becomes positive. An illustration of this case is found in the *p-t* curves of the univariant systems, $K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O + L + V$ (curve 4*b*), and $SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O + L + V$ (curve 2), which proceed from Q_5 to higher temperature and pressure.

26. Coincidence Theorem. On further increase in temperature the liquid will lie on the line, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$-$K_2O \cdot 2SiO_2$, the area A_{12l} becomes zero, and equation (16) becomes

$$\frac{dp}{dt} = \frac{A_{2lv}(\eta' - \eta^l) - A_{1lv}(\eta'' - \eta^l)}{A_{2lv}(v' - v^l) - A_{1lv}(v'' - v^l)}.$$

At this point the curve has the same slope as the common melting-point curve of $(K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2)$, an illustration of the general relation that when a linear relation exists between the composition of *n* or fewer phases, the *p-t* curves of all univariant systems containing these phases coincide. When all the reacting phases have a constant composition, the curves will coincide throughout their course; when the compositions of some or all of them are variable, and they only casually have such a composition that the above linear relation is possible, then the curves are tangent.*

Let us prove this in detail for three phases lying on a straight line in a three-component system. Consider the *p-t* curves of the univariant equilibria, $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P^{IV} + P^{V}$, which proceed from the quintuple point, $P' + P'' + P''' + P^{IV} + P^{V}$. The equation of the first of these is

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* F. A. H. Schreinemakers (*Proc. Acad. Sci. Amsterdam*, **19**, 514–27, (1916) and subsequent papers in the same journal) mentions some special cases of this general theorem.

$$\frac{dp}{dt} = \frac{\begin{vmatrix} \mathrm{H}' & m_1' & m_2' & m_3' \\ \mathrm{H}'' & m_1'' & m_2'' & m_3'' \\ \mathrm{H}''' & m_1''' & m_2''' & m_3''' \\ \mathrm{H}^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} V' & m_1' & m_2' & m_3' \\ V'' & m_1'' & m_2'' & m_3'' \\ V''' & m_1''' & m_2''' & m_3''' \\ V^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}.$$

Now assume that P', P'', P''' lie on a straight line in the composition diagram.* We then have the relation

$$A'P' = A''P'' + A'''P''',$$

and hence also

$$A'm_1' = A''m_1'' + A'''m_1''',$$
$$A'm_2' = A''m_2'' + A'''m_2''',$$

and

$$A'm_3' = A''m_3'' + A'''m_3'''.$$

By substituting these values of m_1', m_2', m_3' in the above determinants, and subtracting A'' times the second row and A''' times the third row from A' times the first row, we get

$$\frac{dp}{dt} = \frac{\begin{vmatrix} A'\mathrm{H}' - A''\mathrm{H}'' - A'''\mathrm{H}''' & 0 & 0 & 0 \\ \mathrm{H}'' & m_1'' & m_2'' & m_3'' \\ \mathrm{H}''' & m_1''' & m_2''' & m_3''' \\ \mathrm{H}^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{\begin{vmatrix} A'V' - A''V'' - A'''V''' & 0 & 0 & 0 \\ V'' & m_1'' & m_2'' & m_3'' \\ V''' & m_1''' & m_2''' & m_3''' \\ V^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}},$$

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* An example of this is found in Fig. 5. Here the phases are $K_2O \cdot 2SiO_2$, $K_2O \cdot 2SiO_2 \cdot H_2O$ and V; the vapor phase contains only H_2O, and its composition is represented by the apex of the component triangle.

which reduces to

$$\frac{dp}{dt} = \frac{(A'H' - A''H'' - A'''H''')\begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}}{(A'V' - A''V'' - A'''V''')\begin{vmatrix} m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \\ m_1^{IV} & m_2^{IV} & m_3^{IV} \end{vmatrix}},$$

or

$$\frac{dp}{dt} = \frac{A'H' - A''H'' - A'''H'''}{A'V' - A''V'' - A'''V'''}.$$

Similarly, the relation between the variations of p and t in the second of the above univariant equilibria, $P' + P'' + P''' + P^V$, reduces to the same expression. It will be observed that the coefficients A', A'', A''' are those that occur in the reaction equation

$$A'P' = A''P'' + A'''P'''.$$

Hence we see that whenever three phases lie on a straight line in the composition diagram, the p-t curves of all ternary equilibria containing these three phases coincide with each other and with the p-t curve of the univariant binary equilibrium between the three phases alone.

27. Equilibrium, $K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2$ *+ Solution + Vapor.* We will now consider the application of our equation to a different type of equilibrium between two solids, liquid and vapor. Consider the equilibrium, $K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + L + V$ (curve $7b + 7c$). In the concentration diagram the course of this equilibrium is the curve Q_2Q_4, the boundary curve between the fields of $K_2O \cdot 2SiO_2$ and $K_2O \cdot 2SiO_2 \cdot H_2O$. Since the two solid phases and vapor lie on a straight line, the equation becomes

$$\frac{dp}{dt} = \frac{A_{2vl}\,(\eta' - \eta^v) - A_{1vl}\,(\eta'' - \eta^v)}{A_{2vl}\,(v' - v^v) - A_{1vl}\,(v'' - v^v)},$$

in which P' and P'' represent $K_2O \cdot 2SiO_2$ and $K_2O \cdot 2SiO_2 \cdot H_2O$, respectively. This is the equation of the dissociation-pressure curve of $K_2O \cdot 2SiO_2 \cdot H_2O$. Hence, as we saw before, the *p-t* curves of the equilibrium, $K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + L + V$, coincide with the dissociation-pressure curve of $K_2O \cdot 2SiO_2 \cdot H_2O$. The slope of this curve will remain positive as we go along the boundary curve, $K_2O \cdot 2SiO_2$-$K_2O \cdot 2SiO_2 \cdot H_2O$, and will not show anything special until the liquid phase falls on the line, V-$K_2O \cdot 2SiO_2$. But here the two triangles A_{234} and A_{134} become zero at the same time, and the equation becomes meaningless. This point corresponds to the termination of the curve at the quadruple point, $K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + L + V$ in the binary system, H_2O-$K_2O \cdot 2SiO_2$. When the liquid has crossed the line, H_2O-$K_2O \cdot 2SiO_2$ the areas of all the triangles change sign, hence dp/dt remains positive, and with decreasing temperature we retrace the same *p-t* curve to the quintuple point Q_4. This portion of the curve also corresponds to the equilibrium, $K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + V$.

In the first equilibrium considered, the univariant equilibrium, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot SiO_2 + L + V$, the assumption that the vapor phase is pure H_2O was practically without influence; the vapor phase might contain appreciable quantities of either K_2O or SiO_2 or both without appreciably affecting the course of the *p-t* curve. The only effect would be a slight diminution of the areas A_{1lv} and A_{2lv}, the coefficients of $(\eta'' - \eta^l)$ and $(v'' - v^l)$, and of $(\eta' - \eta^l)$ and $(v' - v^l)$, respectively. In the second case, however, the assumption is of importance; only in the improbable case that the ratio of SiO_2/K_2O in the vapor is the same as in the solid, i.e., 2/1, would it still be true that the equilibrium, $K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + L + V$, coincides with the equilibria $K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + V$ and $K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2 \cdot H_2O + V$, and with the dissociation-pressure curve of $K_2O \cdot 2SiO_2 \cdot H_2O$. In case the vapor contained a small amount of K_2O, the curve, $K_2O \cdot 2SiO_2 + K_2O \cdot 2SiO_2 \cdot H_2O + L + V$, would consist of two parts, one on one side, the other on the other side, of the dissociation-pressure curve, and the two parts would join at the top in a smooth curve, whose point of maximum temperature would be found at the point where the entropy change in the reaction passes through zero, hence on the K_2O side of the line, $K_2O \cdot 2SiO_2$ - $K_2O \cdot 2SiO_2 \cdot H_2O$. But unless the K_2O content of the vapor is large, which is improbable, the effect will be small; the area, $K_2O \cdot 2SiO_2$ - $K_2O \cdot 2SiO_2 \cdot H_2O$ - V, instead of being zero, will be a very small quantity which will have but a slight influence on the above relations; the curves, instead of coinciding, would lie very close to each other.

28. Equilibrium, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot SiO_2$ + *Solution* + *Vapor.* All the *p-t* curves so far discussed have had their end-points inside the component triangle; all of them have gone from one quintuple point to another. Let us now consider one which goes from a quintuple point to a quadruple point in one of the limiting binary systems, e.g., the curve, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (curve 10*b*), which goes from quintuple point Q_1 to the quadruple point, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$, in the binary system, H_2O-$K_2O \cdot SiO_2$. Since the phases, V, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, and $K_2O \cdot SiO_2$, lie on a straight line, the area of the triangle, V-$K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$-$K_2O \cdot SiO_2$, is zero, and the equation of the *p-t* curve reduces to

$$\frac{dp}{dt} = \frac{A_{2vl}(\eta' - \eta'') - A_{1vl}(\eta' - \eta'')}{A_{2vl}(v' - v'') - A_{1vl}(v' - v'')},$$

in which the accents (′) and (″) refer to the solid phases, $K_2O \cdot SiO_2$ and $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, respectively. This is evidently the dissociation-pressure curve of $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$; in harmony with our previous conclusions, the slope of the curve, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (10*b*), is the same as that of the dissociation-pressure curve of $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ (10*a* + 10*b*). At the quintuple point it is evident that both numerator and denominator are negative, dp/dt therefore positive. Also, the denominator being much larger than the numerator, the numerical value of dp/dt is less than unity. As the liquid approaches the side of the component triangle along the boundary curve, both the triangles A_{2vl} and A_{1vl} diminish in size in about the same proportion, and the value of dp/dt will not change materially. When the liquid gets on the line, H_2O-

$K_2O \cdot SiO_2$, both triangles become zero simultaneously, and the equation becomes indeterminate; the curve is at its end point at the quadruple point in the binary system.

It is evident that when the phases have the composition indicated above, no maximum is possible in the *p-t* curve of the univariant equilibrium. However, if the vapor phase, instead of being pure H_2O, contained a small amount of SiO_2, the curve would have a horizontal tangent before the phases, L, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, and $K_2O \cdot SiO_2$ fell on a straight line, as can readily be seen from the equation of the curve.

29. Equilibrium, $K_2O \cdot 2SiO_2$ + $K_2O \cdot 4SiO_2 \cdot H_2O$ + Solution + Vapor. In the discussion of binary systems, it was seen that when a volatile component is considered, the maximum temperature is not at the composition of a compound, as in condensed systems, but is displaced in the direction of the more volatile component. A similar condition is found in the general case; an example in a ternary system is found along the curve, $K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O + L + V$ (curve 4*b*), which goes from Q_4 to Q_{5a}. The equation of this curve is

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \dfrac{A_{1lv}}{A_{12l}}(\eta' - \eta^l) - \dfrac{A_{1lv}}{A_{12l}}(\eta'' - \eta^l)}{(v^l - v^v) + \dfrac{A_{1lv}}{A_{12l}}(v' - v^l) - \dfrac{A_{1lv}}{A_{12l}}(v'' - v^l)},$$

in which the accents (′) and (″) refer to the phases, $K_2O \cdot 2SiO_2$ and $K_2O \cdot 4SiO_2 \cdot H_2O$, respectively. The condition for a temperature maximum is that the denominator of this expression shall approach zero as a limit; *dp*/*dt* becomes infinite. Since the volume difference between vapor and liquid is far greater than that between solid and liquid, the denominator will approach zero as a limit only when the coefficients of the last two volume differences become very large, hence when the area of the triangle, $K_2O \cdot 2SiO_2$-$K_2O \cdot 4SiO_2 \cdot H_2O$-L, becomes very small. This point will be reached slightly before the liquid phase lies on the line, $K_2O \cdot 2SiO_2$-$K_2O \cdot 4SiO_2 \cdot H_2O$, hence the point of maximum temperature has been displaced slightly in the direction of the volatile component.

30. The Order of p-t Curves around an Invariant Point. In the general consideration of phase equilibria it is convenient to proceed from a consideration of the invariant points to the various univariant equilibria which proceed therefrom, and to consider the sequence of the *p-t* curves around the invariant point. Such a course is often of great value in determining the stable phases in an investigation of complex systems. The order* of the *p-t* curves may be deduced from the theorem that whenever a linear relation exists between n of the $n + 1$ phases in a univariant equilibrium, the *p-t* curves of all the univariant systems containing these phases coincide. But these curves extend in both directions from the invariant point; in one direction the equilibrium under consideration will be stable, in the other, metastable, and to tell the actual position of any curve, or to distinguish between the stable and metastable portions of any one curve, a knowledge of the entropy and volume changes is necessary. However, it will be shown that two adjoining curves, i.e., curves that are not separated by either the stable or metastable portions of other curves, e.g., the *p-t* curves of the univariant ternary equilibria, $P' + P'' + P''' + P^{IV}$ and $P' + P'' + P''' + P^{V}$, will coincide in their stable portions, that is, are stable in the same direction from the invariant point, when the phases P^{IV} and P^{V} lie on opposite sides of the straight line $P'P''P'''$, and *vice versa*. With the aid of these theorems and general considerations to be discussed later the actual position of the *p-t* curves may be fixed within certain limits.

The above theorem may be proved as follows. From the definition of the chemical potential μ, if the μ of a substance in a given phase is greater than the μ of the same substance in another phase, the two phases are not in equilibrium with respect to that substance and it will tend to pass from the phase in which its chemical potential is the greater into that phase in which its chemical potential is the less. At the triple point, ice + water + vapor in the one-component system,

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* By "the order of the *p-t* curves" is meant the sequence in which we shall cut the curves as we circle around the invariant point, with the stipulation that reversing the direction of rotation reverses the sequence but not the order.

H_2O, the chemical potential of H_2O in all three phases is the same. If we simultaneously change the pressure and temperature so as to proceed along any one of the three p-t curves that intersect at the triple point, one of the phases will disappear. By making these changes we have given greater increments to the chemical potential of the phase that disappears than to the chemical potentials of the other two phases; the chemical potential of water remains equal in these two phases since we, by hypothesis, have made such changes of pressure and temperature as to proceed along the p-t curve of stable coincidence of these phases.

The fundamental equations of the form of (1) [97] for the three phases that coexist at the triple point are

$$\begin{aligned} V^v dp &= \mathrm{H}^v dt + m^v d\mu^v, \\ V^l dp &= \mathrm{H}^l dt + m^l d\mu^l, \\ V^s dp &= \mathrm{H}^s dt + m^s d\mu^s, \end{aligned}$$

in which the indices v, l, s refer to the vapor, liquid, and solid phases. Each of these equations may be divided by the mass m of the phase; in the resulting equations

$$\begin{aligned} v^v dp &= \eta^v dt + d\mu^v, \\ v^l dp &= \eta^l dt + d\mu^l, \\ v^s dp &= \eta^s dt + d\mu^s, \end{aligned}$$

the volume and entropy terms refer to the specific volume and entropy of each phase.

Now if, as stated above, we proceed along the p-t curve of the condensed system, ice-liquid, which is one of the p-t curves that intersect at the triple point, we can obtain a value for $d\mu$, the differential of the chemical potential, from the two equations of the type of (1) [97] referring to the liquid and solid phases, by solving the two equations for dt in terms of dp, which will give us

$$dt = \frac{v^l - v^s}{\eta^l - \eta^s}\, dp,$$

and substituting this value of dt in one of the original equations

Substituting in the equation referring to the liquid phase, we get

$$d\mu^l = \left[v^l - \eta^l \frac{v^l - v^s}{\eta^l - \eta^s} \right] dp.$$

Similarly, the value of $d\mu^v$ in the stable direction of the curve, is given by

$$d\mu^v = \left[v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s} \right] dp.$$

Now since, by hypothesis, we have proceeded in the direction of the stable portion of the curve, ice + liquid,

$$d\mu^v > d\mu^l.$$

Hence

$$dp \left[\left(v^v - \eta^v \frac{v^l - v^s}{\eta^l - \eta^s} \right) - \left(v^l - \eta^l \frac{v^l - v^s}{\eta^l - \eta^s} \right) \right] > 0,$$

which reduces to

$$\frac{dp\, [(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{\eta^l - \eta^s} > 0,$$

one form of the condition for stability of the equilibrium solid + liquid.

When we consider the actual magnitude of the various terms in this equation we see that the coefficient of dp in the numerator is necessarily positive. All the individual terms $(v^v - v^l)$, $(\eta^l - \eta^s)$, $(\eta^v - \eta^l)$ and $(v^l - v^s)$ are of necessity positive except the last one, the volume change of melting of ice, which is negative. But the last term is affected by the negative sign, hence the term as a whole is positive, and the coefficient of dp has a positive sign.* The equilibrium in question will then be stable as the pressure is increased from the invariant point when the denominator is positive; $(\eta^l - \eta^s)$ is of necessity positive, hence the equilibrium, ice + liquid, is stable with increasing pressure from the invariant point; on decreasing the pressure we pass on to the metastable portion of the curve, into a region where vapor is stable.

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* The case that $(v^l - v^s)$ is negative is, of course, exceptional. But in any case, the coefficient of dp is positive, since the two entropy changes are of the same order of magnitude, while the volume change on evaporation is many times larger than the volume change on melting.

By solving for dp in the above equations of the type of (1) [97] referring to the solid and liquid phases, we get a similar inequality,

$$\frac{dt\,[(v^v - v^l)(\eta^l - \eta^s) - (v^l - v^s)(\eta^v - \eta^l)]}{v^l - v^s} > 0,$$

which gives the condition for stability with change in temperature. It will be observed that the condition for temperature stability differs from the condition for pressure stability in having dt in place of dp in the numerator, and in having $(v^l - v^s)$ in place of $(\eta^l - \eta^s)$ in the denominator. Since the coefficient in the numerator is unchanged, it is always positive; the equilibrium, solid + liquid, is stable with increasing temperature when the denominator is positive, and is stable with decreasing temperature when the denominator is negative. In the exceptional case of H_2O, this volume change is negative, hence the equilibrium, ice + liquid, is stable with decreasing temperature from the triple point; on increasing the temperature we pass on to the metastable portion of the curve, into a region in which vapor is stable.

31. Generalized Theorem Concerning the Order of p-t Curves around an Invariant Point. The above reasoning may be generalized as follows. At an invariant point, if the differentials satisfy the $(n + 1)$ equations of the type of (1) [97] for the univariant equilibrium, $P' + P''' + P^{IV} \ldots + P^{n+1} + P^{n+2}$ (in which phase P'' is missing), we will move along the p-t curve of this equilibrium. In one direction from the invariant point the missing phase P'' will be stable, in the other direction phase P'' will be unstable. In the first case, we will be on the metastable prolongation of the p-t curve, in the second case, we will be on the stable portion of the p-t curve. The condition that a given phase in a one-component system is unstable was found to be that its chemical potential is greater than the chemical potential of the stable coexisting set of phases, which condition is represented by the inequality

$$Vdp - \mathrm{H}dt > m_1 d\mu_1 + m_2 d\mu_2 \ldots + m_n d\mu_n.$$

Similarly, the condition that the equilibrium

$$P'' + P''' + \mathrm{P}^{IV} \ldots + P^{n+1} + P^{n+2}$$

is stable is that the missing phase P' is unstable.

By solving the $(n + 1)$ equations of the type of (1) [97], referring to the $(n + 1)$ coexisting phases of the equilibrium in which P'' is the missing phase, for $d\mu_1$, $d\mu_3$, $d\mu_4$, and dt in terms of dp, and substituting in the above inequality, (the quantities V, H, m_1, m_3, $\ldots$ m_n referring to phase P'') the stability is found to depend upon the sign of the following expression:

$$\frac{dp\begin{vmatrix} \mathrm{H}' & V' & m_1' & m_2' & m_3' & \text{—} & \text{—} & m_n' \\ \mathrm{H}'' & V'' & m_1'' & m_2'' & m_3'' & \text{—} & \text{—} & m_n'' \\ \mathrm{H}''' & V''' & m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ \mathrm{H}^{IV} & V^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \text{—} & \text{—} & m_n^{IV} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \mathrm{H}^{n+1} & V^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ \mathrm{H}^{n+2} & V^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}}{\begin{vmatrix} \mathrm{H}' & m_1' & m_2' & m_3' & \text{—} & \text{—} & m_n' \\ \mathrm{H}''' & m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ \mathrm{H}^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \text{—} & \text{—} & m_n^{IV} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \mathrm{H}^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ \mathrm{H}^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}} \qquad \text{(A)}$$

The equilibrium, $P' + P''' + P^{IV} \ldots + P^{n+1} + P^{n+2}$, will be stable if this expression is negative, and *vice versa*. Also the univariant equilibrium, $P'' + P''' \ldots + P^{n+1} + P^{n+2}$, in which P' is the missing phase, is stable when the expression

$$\frac{dp\begin{vmatrix} H' & V' & m_1' & m_2' & m_3' & \text{—} & \text{—} & m_n' \\ H'' & V'' & m_1'' & m_2'' & m_3'' & \text{—} & \text{—} & m_n'' \\ H''' & V''' & m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ H^{IV} & V^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \text{—} & \text{—} & m_n^{IV} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ H^{n+1} & V^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ H^{n+2} & V^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}}{\begin{vmatrix} H'' & m_1'' & m_2'' & m_3'' & \text{—} & \text{—} & m_n'' \\ H''' & m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ H^{IV} & m_1^{IV} & m_2^{IV} & m_3^{IV} & \text{—} & \text{—} & m_n^{IV} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ H^{n+1} & m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ H^{n+2} & m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}} \qquad \text{(B)}$$

is positive.

The numerators of the two expressions given above are identical. When a linear relation exists between the phases, P''', P^{IV}, . . . P^{n+1}, P^{n+2}, the denominators reduce to

$$\Delta\text{H}\begin{vmatrix} m_1' & m_2' & m_3' & \text{—} & \text{—} & m_n' \\ m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}, \qquad \text{(C)}$$

and

$$\Delta\text{H}\begin{vmatrix} m_1'' & m_2'' & m_3'' & \text{—} & \text{—} & m_n'' \\ m_1''' & m_2''' & m_3''' & \text{—} & \text{—} & m_n''' \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ m_1^{n+1} & m_2^{n+1} & m_3^{n+1} & \text{—} & \text{—} & m_n^{n+1} \\ m_1^{n+2} & m_2^{n+2} & m_3^{n+2} & \text{—} & \text{—} & m_n^{n+2} \end{vmatrix}, \qquad \text{(D)}$$

in which ΔH denotes the entropy change which takes place when these n phases, P''', P^{IV}, . . . P^{n+1}, P^{n+2}, react.

It will be observed that these two expressions are identical except for the first row of the determinants, which in (C) contains the composition terms of phase P', and in (D) contains the composition terms of phase P''. Hence it is evident that the numerical values of expressions (A) and (B) will be the same, i.e., the two curves will be stable in the same direction from the invariant point, when (C) and (D) have opposite signs (since (A) and (B) have opposite signs). But (C) and (D) will have opposite signs only when phases P' and P'' lie on opposite sides of the onefold P''', P^{IV}, ... P^{n+1}, P^{n+2}. In a two-component system this onefold is a point; in a three-component system, a line; in a four-component system, a plane, etc.

The above may be summarized as follows: When two adjoining *p-t* curves (which represent the relation between the variations in pressure and temperature in two different univariant equilibria between $n + 1$ phases in a system of n components) coincide, owing to a linear relation being possible between the compositions of the n phases common to both equilibria, i.e., to these n phases lying on the onefold n, whose position is determined by the above linear relation, these equilibria are stable in the same direction from the invariant point, i.e., their stable portions coincide, when the other two phases lie on opposite sides of the onefold n. By "the other two phases" is meant the phases, one in each of the univariant equilibria, which do not lie on the onefold n. In a two-component system, the onefold n is a point; in a three-component system, a line; in a four-component system, a plane, etc. This has been proved for the case that a linear relation exists between the compositions of n of the $(n + 2)$ phases that coexist at the invariant point. The cases where a linear relation exists between the composition of $(n - 1)$, $(n - 2)$, ... $(n - a)$, phases may be regarded as special cases.

32. Generalizations Concerning p-t Curves. Before illustrating the application of the above principles to actual cases, certain generalizations will be made concerning the *p-t* curves from the state of aggregation of the phases. The actual value of dp/dt for any univariant equilibrium is given by equation (6) [129], which, as will be shown later, is equivalent to

$$\frac{dp}{dt} = \frac{\Delta \mathrm{H}}{\Delta V},$$

in which ΔH is the entropy change, ΔV the volume change of the reaction in question. Whenever we have a reaction in which the vapor does not take part, e.g., the reaction

$$\mathrm{S}' + \mathrm{S}''' = \mathrm{S}'' + \mathrm{L},$$

the slope of the *p-t* curve is always very great, because of the small value of ΔV. In other words, the *p-t* curves of all condensed systems are almost vertical, and go from the invariant point to regions of higher pressure, and in almost all cases, higher temperature. When the reaction is one between solid phases and vapor, e.g., the dissociation-pressure curve of S′,

$$\mathrm{S}' = \mathrm{S}'' + \mathrm{V},$$

the *p-t* curve always goes from the invariant point to regions of lower temperature and pressure; since ΔV is large (except under high pressure), the slope of the curve is comparatively small. In reactions of the type

$$\mathrm{S}' + \mathrm{L} = \mathrm{S}'' + \mathrm{V},$$

in which both liquid and vapor take part, dp/dt may be large or small, positive or negative. We will consider this case in detail later.

Consider now the application of the above principles to the determination of the sequence of *p-t* curves around an invariant point.* The method used is based on the fact that the order of the slopes dp/dt of the various curves at the invariant point is determined by the masses of the phases which take part in the various univariant reactions. This is evident from equation [129] or from the expanded form of (6) [129] given below. The method of applying this criterion is by considering what curves will coincide when we vary the composition of different phases. If by varying the composition of one phase in a certain direction n phases get on the onefold (n), then, as proved above, the p-t curves of the two univariant equilibria formed by these n phases with each of the other two phases will coincide; these two curves must be adjoining curves, and no other curves can be between them. By repeating this reasoning, assuming the composition of the same phase to change in other directions, or assuming the composition of another phase to change, the relative positions of the p-t curves, i.e., the order in which they succeed one another around the invariant point, can be deduced. The stable and metastable portions can be distinguished by means of the theorems previously given.

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* The question of the sequence of *p-t* curves around an invariant point has been discussed by A. Smits (*Proc. Acad. Sci. Amsterdam*, **18**, 800–804 (1916)), and by F. A. H. Schreinemakers in the series of papers beginning with *Proc. Acad. Sci. Amsterdam*, **18**, 116–26 (1916), and by G. W. Morey and E. D. Williamson, *J. Am. Chem. Soc.*, **40**, 59 (1918).

33. Order of the p-t Curves in the Ternary System, H_2O-$K_2O \cdot SiO_2$-SiO_2. Let us apply the above considerations to the quintuple points in the ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2, and pay particular attention to the question of the sequence of the p-t curves around the invariant (quintuple) point. For the purpose of this discussion, we will combine the above theorems in regard to the conditions under which p-t curves coincide, and in regard to the factors which determine whether the curves coincide stable to stable or stable to metastable, in the following rule: Whenever in a ternary system three phases lie on a straight line, the p-t curves of all the ternary univariant equilibria containing these three phases coincide with each other and with the p-t curve of the univariant binary equilibrium between the three phases alone. When the other two phases at the quintuple point lie on the same side of the line on which lie the compositions of the three reacting phases, the curves coincide stable to metastable; when the other two phases lie on opposite sides of the line on which lie the compositions of the three reacting phases, the curves coincide stable to stable.

The compositions of all the phases which are met with in the ternary system, H_2O-$K_2O \cdot SiO_2$-SiO_2, are shown in Fig. 6. In treating this system we will assume that the vapor phase contains H_2O only. The presence of K_2O in the vapor has been detected,* but the amount was very small. The boundary curves show the change in composition of the liquid phase in the univariant equilibria, $S' + S'' + L + V$, as we pass from quintuple point to quintuple point, or from quintuple point to quadruple point, in the limiting binary systems. The composition of the liquid phase at each quintuple point is given by the point of intersection of three boundary curves; these points are designated by the letters Q_1, Q_2, etc. The *p-t* curves experimentally determined are shown in Fig. 7. Figure 8 is a diagrammatic representation of the *p-t* curves, which is easier to follow.

At quintuple point Q_1 we have the three solid phases, $K_2O \cdot SiO_2$, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, and $K_2O \cdot 2SiO_2$, the liquid phase whose composition is given by the point Q_1, and the vapor phase, whose composition is given by the H_2O apex of the component triangle (Figs. 5, 6). Since $K_2O \cdot SiO_2$, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ and V lie on a straight line, the curves, $K_2O \cdot 2SiO_2 + K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + V$ (curve 10*a*)† and $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (curve 10*b*), will coincide; metastably, since the phases, $K_2O \cdot 2SiO_2$ and L, lie on the same side of the line, V-$K_2O \cdot SiO_2$. These two curves also coincide with the dissociation-pressure curve of $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ in the binary system, H_2O-$K_2O \cdot SiO_2$ (curve 10*a* + 10*b*), Fig. 7, hence their position is as shown.

If the compositions of the phases were such that V, L, and $K_2O \cdot 2SiO_2$ lay on a straight line, the *p-t* curves of the univariant equilibrium, $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (curve 6*d*), would coincide, metastably, with the *p-t* curve, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L + V$ (curve 6*c*); if the phases V, L, $K_2O \cdot SiO_2$ lay on a straight line, the curve, $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (curve 6*d*), would coincide, stably, with the curve, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (curve 10*b*). Hence curve, $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (6*d*), must lie between the metastable prolongation of curve, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L + V$ (6*c*), and the stable portion of $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (10*b*). The position of the latter curve being fixed, the position of the curves, $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (6*d*) and $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L + V$ (6*c*), must either be as shown at Q_1, Fig. 7, or the position of these curves in regard to the curves, $K_2O \cdot 2SiO_2 + K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + V$ (10*a*) and $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (10*b*), must be reversed. That the latter arrangement cannot be correct is shown by the fact that if $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ - L - $K_2O \cdot 2SiO_2$ all lay upon a straight line, the curve, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L + V$ (6*c*), would coincide with the curve, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L$, the *p-t* curve of the condensed system. But such a coincidence is possible only with the arrangement shown in Fig. 7; the reversed arrangement cannot be the correct one.

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* Consult the discussion of this point on p. 1210 of the paper: G. W. Morey and C. N. Fenner, *J. Am. Chem. Soc.*, **39**, 1173 (1917).

† The curves are numbered as in Figs. 5, 6, 7, and 8. In Fig. 6 only curves of the type $S' + S'' + L + V$ are shown. In Fig. 8 the *p-t* curves of the condensed systems are not numbered; their position is obvious.

In order to show further the relation between the composition diagram and the *p-t* diagram, let us consider under what conditions the curves, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L$ (the *p-t* curve of the condensed system) and $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (6*d*), will coincide stably. For this coincidence to take place, it is necessary that the phases, L, $K_2O \cdot SiO_2$ and $K_2O \cdot 2SiO_2$, lie on a straight line in the composition diagram (Fig. 6), which intersects internally the line, V-$K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$. On reference to Fig. 6 we see that before the phases can take on the position mentioned above, it will be necessary for the phases, $K_2O \cdot SiO_2$, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ and $K_2O \cdot 2SiO_2$, then the phases, V, L, and $K_2O \cdot SiO_2$, to fall on straight lines. But in the *p-t* diagram, the first of these will result in the curves, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L$ and $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + V$ (10*a*), approaching each other, coinciding, then again diverging, having changed places. Similarly, as a result of the second triplet of phases getting on a straight line, the curves, $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (6*d*) and $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + L + V$ (10*a*) will change places. The curves, $K_2O \cdot SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O + K_2O \cdot 2SiO_2 + L$ and $K_2O \cdot SiO_2 + K_2O \cdot 2SiO_2 + L + V$ (6*d*), now lie next to each other, their stable portions adjoining, and when the phases, L, $K_2O \cdot SiO_2$, and $K_2O \cdot 2SiO_2$, fall on a straight line these two curves will coincide in their stable portions.

The quintuple point Q_3 is exactly similar to Q_1, but instead of $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, $K_2O \cdot SiO_2$, and $K_2O \cdot 2SiO_2$ we have $K_2O \cdot SiO_2 \cdot H_2O$, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$, and $K_2O \cdot 2SiO_2 \cdot H_2O$, respectively. Making these substitutions, the discussion of Q_1 will apply to Q_3.

Quintuple points Q_2 and Q_4 also are similar to each other. Both contain the same three phases, V, $K_2O \cdot 2SiO_2 \cdot H_2O$, and $K_2O \cdot 2SiO_2$. At Q_2 we also have the liquid represented by the point Q_2 and the solid phase, $K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$; at Q_4 we have the liquid represented by the point Q_4 and the solid phase, $K_2O \cdot 4SiO_2 \cdot H_2O$. Since in both systems the phases, V, $K_2O \cdot 2SiO_2 \cdot H_2O$, and $K_2O \cdot 2SiO_2$, lie on a straight line, the curve, $V + K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + K_2O \cdot SiO_2 \cdot \frac{1}{2}H_2O$ ($7a$), which proceeds from Q_2 to lower temperatures and pressures, and the curve, $V + K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O$ ($7b + 7a$), which proceeds from Q_4 to lower temperature and pressure, and the curve, $V + L + K_2O \cdot 2SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2$ ($7b + 7c$), which proceeds from both Q_2 and Q_4 to higher temperatures and pressures, coincide with each other and with the dissociation-pressure curve of $K_2O \cdot 2SiO_2 \cdot H_2O$ in the binary system, H_2O-$K_2O \cdot 2SiO_2$ (curve $7a + 7b + 7c$). The positions of the other curves that proceed from Q_2 and Q_4 are easily found by the same mode of reasoning as that applied to the curves at Q_1.

The quintuple points Q_{5a} and Q_{5b}* differ from the preceding ones in that in each the liquid phase lies inside the triangle formed by the coexisting solid phases, and hence they are both eutectics. At Q_{5a} the coexisting phases are $V + L + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2$, and the liquid lies within the triangle, $K_2O \cdot 4SiO_2 - K_2O \cdot 4SiO_2 \cdot H_2O - K_2O \cdot 2SiO_2$; and, similarly, at Q_{5b} the liquid lies within the triangle, $K_2O \cdot 4SiO_2 \cdot H_2O - K_2O \cdot 4SiO_2 - SiO_2$. Since the liquid is symmetrically placed with regard to the three solid phases, the four univariant equilibria containing liquid will be stable in the same direction from the invariant point. Since $V - K_2O \cdot 4SiO_2 \cdot H_2O - K_2O \cdot 4SiO_2$ is a straight line, the *p-t* curves of the equilibria, $V + L + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$ and $V + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2$, will coincide metastably with each other, and will coincide with the binary equilibrium, $V + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$, the dissociation-pressure curve of $K_2O \cdot 4SiO_2 \cdot H_2O$. Hence the *p-t* curve of $V + L + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$, and therefore of all those containing liquid, will go to higher temperatures and pressures. Since only a small change in liquid composition will make $K_2O \cdot 2SiO_2 - L - K_2O \cdot 4SiO_2 \cdot H_2O$ a straight line, with V and $K_2O \cdot 4SiO_2$ on opposite sides, the curves, $V + L + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O$ and $L + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O$ (the condensed system), will coincide stable to stable, and with a continuous change in the same direction in the liquid composition the curves will cross. Similar reasoning applied to the phases, liquid, $K_2O \cdot 4SiO_2$, and $K_2O \cdot 4SiO_2 \cdot H_2O$, shows that the curve, $V + L + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O$, must lie between the curves, $L + K_2O \cdot 2SiO_2 + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$ and $V + L + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$; and the latter curve must coincide with the dissociation-pressure curve of $K_2O \cdot 4SiO_2 \cdot H_2O$, the equilibrium, $V + K_2O \cdot 4SiO_2 \cdot H_2O + K_2O \cdot 4SiO_2$.

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* The compound, $K_2O \cdot 4SiO_2$, was not met with in the original study of the ternary system, by Morey and Fenner (*J. Am. Chem. Soc.*, **39**, 1173 (1917)), but was found later in the study of the anhydrous binary system by Kracek, Bowen, and Morey (*J. Phys. Chem.*, **33**, 1857 (1929)). The evidence in both studies makes it probable, though not certain, that $K_2O \cdot 4SiO_2 \cdot H_2O$ has a congruent melting point. The relations around quintuple points Q_{5a} and Q_{5b} are thus in part hypothetical, and in Fig. 8 the two invariant points are not separated, nor are the two curves from Q_{5a} and Q_{5b} to the sides of the diagram. The eutectics containing $K_2O \cdot 4SiO_2$ in the binary system, K_2O-SiO_2, are at 752° and 69 weight per cent silica, and at 764° and 72 per cent silica.

Similar reasoning will serve to place the sequence of *p-t* curves around the other eutectic, the invariant point Q_{5b}. The noteworthy feature of the curves proceeding from Q_{5b} is the rapid rise in pressure in the univariant equilibrium, $V + L + K_2O \cdot 4SiO_2 \cdot H_2O + SiO_2$.

In the preceding discussion it has been shown how the fundamental thermodynamic equations developed by Gibbs not only lead to the qualitative generalization known as the Phase Rule, but also afford a direct and detailed treatment of problems of heterogeneous equilibrium. Such an analytical treatment is illustrated for systems of two and three components. In simpler systems it has the advantage of stressing the fundamental relationships that determine the course of equilibrium, in contrast to the graphical method in which these fundamentals may be overlooked in a geometrical maze. With increasing number of components the geometrical methods become increasingly involved, and the analytical method outlined above offers the most hopeful procedure for developing the theory of phase equilibrium in multi-component systems.

H

THE GRAPHICAL REPRESENTATION OF EQUILIBRIA IN BINARY SYSTEMS BY MEANS OF THE ZETA (FREE ENERGY) FUNCTION

[*Gibbs, I, pp. 115–129*]

F. A. H. SCHREINEMAKERS

I. Introduction

1. In the section entitled *Geometrical Illustrations* (pp. 115–129 of the "Equilibrium of Heterogeneous Substances") Gibbs indicates how a general geometrical treatment of phase equilibria can be based on the properties of the thermodynamic functions. A full account of this geometrical method and its subsequent developments would require an exposition of the whole subject of generalised graphical thermodynamics. Since such a comprehensive treatment is not possible in this Commentary, it is hoped that the following discussion of certain equilibria in two-component (binary) systems will serve to illustrate and explain the important geometrical method initiated by Gibbs, and introduce the student to the study of graphical thermodynamics based on the properties of the free energy function ζ.

II. The ζ-x Diagram and the ζ-Curve (Free Energy Curve)

2. Let us represent the composition of a phase containing the two components W and X thus: x mols $X + (1 - x)$ mols W. We shall call this quantity, which contains *in toto* 1 mol, the *unit quantity* of the phase. Then m unit quantities of the phase contain mx mols X and $m(1 - x)$ mols W. Now the ζ-value of a phase is determined by its temperature t, its pressure p, its composition x, and its quantity m (units). Unless mentioned otherwise, however, we shall mean by the ζ of a phase the ζ of unit quantity of this phase. The ζ of m units will then be $m\zeta$, provided that the total energy, total entropy and total volume of the phase are first degree homogeneous functions of the mass variables. This proviso means that we assume we can neglect the surface effects which enter into the consideration of *micro-heterogeneous* systems. For given t and p, the ζ of a phase will depend, therefore, only on its composition. In the case of a binary system this composition is defined by the value of x (the composition parameter).

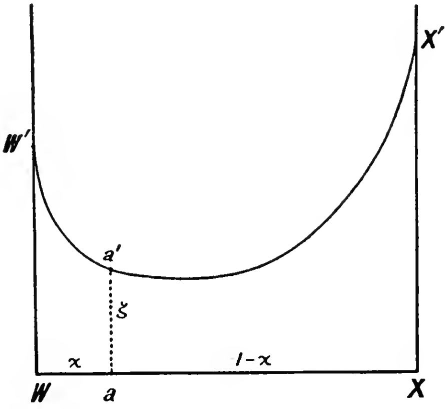

FIG. 1

In Fig. 1, in which $WX = 1$, the point a represents a phase containing $Wa (= x)$ mols X and $aX (= 1 - x)$ mols W. If we now draw the ordinate aa' equal to the ζ of this phase, we shall call the point a' the ζ-point of the phase a. If we give all compositions, from pure W to pure X, to the phase a, then the point a runs along the line WX, whilst the point a' traverses a curve $W'a'X'$, which, at constant t and p is called the ζ-curve (free energy curve). Clearly W' is the ζ-point of the pure substance W and X' the ζ-point of the pure substance X. It can be shown that the ζ-curve touches the lines WW' and XX' at the points W' and X' respectively (for proof see note at the end of this article).

When all points of WX represent liquids, then $W'a'X'$ is the ζ-curve of these liquids, whilst W' and X' are the ζ-points of the pure liquids and a' that of liquid a. When the points of WX represent vapors (gases), then $W'a'X'$ is the ζ-curve of these vapors, whilst W' and X' are the respective ζ-points of the pure vapors W and X and a' that of the binary vapor a. When the points of WX represent homogeneous mixed crystals, then $W'a'X'$ is the ζ-curve of these mixed crystals, whilst W' and X' are the respective ζ-points of the pure solid substances W and X and a' that of the mixed crystalline phase a.

3. We now take two phases A and B with the compositions x_1 mols $X + (1 - x_1)$ mols W, x_2 mols $X + (1 - x_2)$ mols W. If we bring together m_1 units of A and m_2 units of B, and if we suppose that they continue to exist unchanged beside one another, then we have a system or phase complex

$$m_1A + m_2B, \tag{1}$$

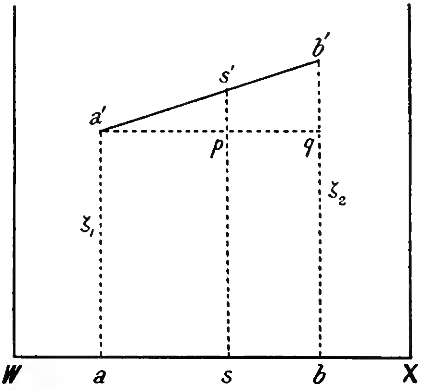

FIG. 2

which may be stable or not. Let its total composition be represented by x mols $X + (1 - x)$ mols W. Since this system contains *in toto* $(m_1 + m_2)$ mols and contains $m_1x_1 + m_2x_2$ mols X, we have

$$x = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}.$$

From this follows

$$m_1(x - x_1) = m_2(x_2 - x). \tag{2}$$

If we imagine the phases A and B and the system represented in Fig. 2 by the points a, b and s, then we have $x_1 = Wa$,

$x_2 = Wb$, $x = Ws$; and $x - x_1 = as$, $x_2 - x = sb$. From (2) it follows that

$$m_1 \times as = m_2 \times sb. \tag{3}$$

If we put (compare Fig. 2) $sb = ab - as$, or $as = ab - sb$, then

$$as = \frac{m_2}{m_1 + m_2} ab, \qquad sb = \frac{m_1}{m_1 + m_2} ab. \tag{4}$$

Thus the position of the point s depends upon the ratio $m_1 : m_2$. When $m_1 = m_2$, $as = sb$, so that point s is situated in the middle of ab; when $m_1 > m_2$, $as < sb$, so that s is closer to point a; when $m_1 < m_2$, s is situated closer to point b.

If we imagine a mass m_1 in point a and a mass m_2 in point b, then it follows from (3) that point s is the centre of gravity of these masses. If we denote the ζ's of the phases A and B by ζ_1 and ζ_2, then the *total* ζ of system (1) is $m_1\zeta_1 + m_2\zeta_2$. If we call the ζ of a unit quantity of this system ζ_s, then we have

$$\zeta_s = \frac{m_1 \zeta_1 + m_2 \zeta_2}{m_1 + m_2}. \tag{5}$$

We now take $aa' = \zeta_1$ and $bb' = \zeta_2$ (see Fig. 2). Then $\zeta_s = ss'$. This can easily be proved. For

$$ss' = sp + ps' = \zeta_1 + ps'. \tag{6}$$

But from the similarity of the triangles $a'ps'$, $a'qb'$ it follows that

$$\frac{ps'}{qb'} = \frac{a'p}{a'q} = \frac{as}{ab} = \frac{m_2}{m_1 + m_2}, \tag{7}$$

and from (7) follows

$$ps' = \frac{m_2}{m_1 + m_2} \times qb' = \frac{m_2}{m_1 + m_2} \times (\zeta_2 - \zeta_1).$$

Substituting this value of ps' in (6),

$$ss' = \frac{m_1 \zeta_1 + m_2 \zeta_2}{m_1 + m_2}. \tag{8}$$

From (5) and (8) we see that $\zeta_s = ss'$.

If we now call s' the ζ-point of the system, then we can state that the ζ-point of system (1) is represented by the centre of gravity of masses m_1 and m_2 at the ζ-points a' and b'. From this it appears that each point of the line $a'b'$ represents the ζ-point of a system (1); the closer this point lies to a' the greater the value of $m_1 : m_2$, the closer to b' the smaller the value of $m_1 : m_2$. For this reason we shall call $a'b'$ the ζ-line of the two-phase system or phase complex $A + B$.

4. According to a theorem of Gibbs, at constant t and p a given quantity of substance arranges itself in such a way that the total ζ is a minimum. Or, of all systems (phases) at constant t and p with the same total composition (in regard to the independent components), that is the most stable one which has the smallest ζ. In order to apply this in the graphical representation, we take a point e (Fig. 3). This point e may represent a *single* phase, e.g., a liquid, a vapor, a mixed crystal, or possibly a compound. The point e may represent also various phase-complexes or systems, e.g., of the phases a and b, or z and u (see Fig. 4). We shall represent all these possible or conceivable phases and systems, which have the same composition e, by E_1, E_2, E_3 etc., and their ζ-points by e', e'', e''' etc. It is clear that all these ζ-points are situated on a vertical line (ordinate) through the point e. Since each of the phases or phase-complexes denoted by E_1, E_2, E_3 etc. contains *in toto* one mol of the components W and X and has the same composition with respect to these components, it follows that each of these phases

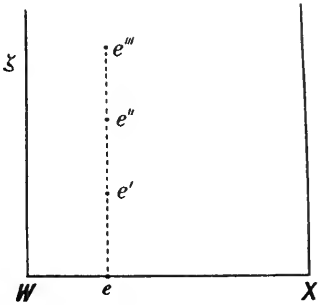

FIG. 3

or phase-complexes (systems) contains the same amounts of the components W and X. As we have taken $ee' < ee'' < ee'''$, and consequently E_1 has the smallest ζ, E_1 is the most stable, according to the theorem of Gibbs mentioned above. Therefore E_3 and E_2 may change into E_1, but the opposite transformation, i.e., of E_1 into E_2 or E_3, is not possible. So in general we may say: of all phases and systems, the ζ-points of which are situated perpendicularly above one another in the (ζ, x)-diagram at constant temperature and pressure, that one is the most stable which possesses the lowest ζ-point. In the following considerations we shall make frequent use of this principle.

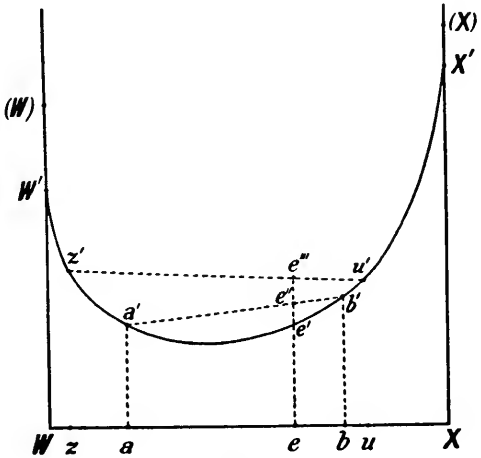

FIG. 4

5. We now assume that the curve $W'X'$ of Figs. 4 and 5 represents the ζ-curve of a series of liquids. This curve may be, as in Fig. 4, at all points convex towards the composition axis, or, as in Fig. 5, partly convex and partly concave. A point e of Fig. 4 may represent not only the single liquid phase e but also an infinite number of systems of two liquids, e.g., of the liquids a and b, or of z and u, etc. We call these the systems $L(a) + L(b)$, or $L(z) + L(u)$, etc. The ζ-point of liquid e is represented by the point e' of the ζ-curve, that of $L(a) + L(b)$ by the point e'' of the line $a'b'$, and that of $L(z) + L(u)$ by the

point e''' of the line $z'u'$. So the transformations

$$L(a) + L(b) \rightarrow L(e)$$

$$L(z) + L(u) \rightarrow L(e)$$

are possible, namely a mixing of the liquids a and b or of z and u to give e. But the opposite changes, i.e., a *separation* of the liquid e into liquids a and b or into liquids z and u, are not possible. Since these considerations apply equally to every liquid e of Fig. 4, it follows that: *when the ζ-curve is wholly convex towards the composition axis, all the liquids are stable and miscible with one another in all proportions.*

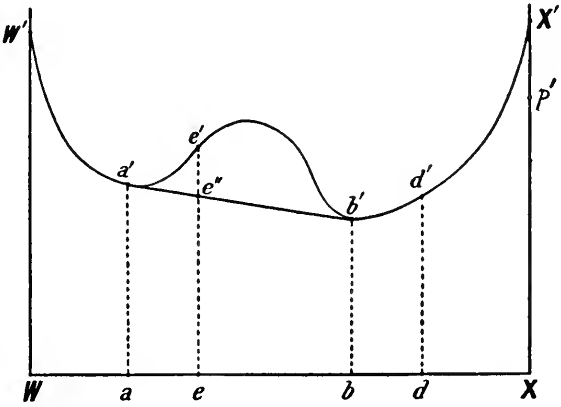

FIG. 5

6. In Fig. 5 we can draw a double tangent line, touching the ζ-curve in points a' and b'. Since the ζ-point e'' of the system $L(a) + L(b)$ now lies *below* the ζ-point e' of the liquid phase e, the conversion $L(e) \rightarrow L(a) + L(b)$ may occur, i.e., a separation of liquid e into the liquids a and b. Conversely, the liquids a and b cannot mix to give the liquid e. Hence we have the following result for Fig. 5. All the liquids of Wa and bX are stable; all the liquids between a and b are metastable or unstable, and separate or tend to separate into the stable system $L(a) + L(b)$. Let us take at ordinary temperature and pressure W = water, X = ether. If we now add so little ether to the water that the former is completely dissolved, we get a solution of ether in water represented by a point of Wa. If we add so little water to ether that the water completely dissolves, we get a solution of water in ether represented by a point of bX. If, however, we bring ether and water together in such a proportion that their mixture is represented by a point between a and b, then no homogeneous liquid is formed, but on the contrary the system, or phase-complex, $L(a) + L(b)$, i.e., a liquid a containing much water and little ether, and a liquid b containing much ether and little water.

7. In relation to the further discussion we shall deduce the foregoing results also in the following way. Every chord we may draw in Figs. 4 and 5 is also the ζ-line of a *conceivable* two-phase system. Thus each point of $a'b'$ represents the ζ-point of a system $L(a) + L(b)$, each point of $z'u'$ the ζ-point of a system $L(z) + L(u)$, etc. So we may imagine an infinite number of ζ-points on every arbitrary vertical line; the lowest ζ-point of every vertical line represents a stable state. Of all the ζ-points we can imagine in Fig. 4 on a vertical line, the point of intersection with the ζ-curve is lowest, and hence it follows that of all conceivable ζ-points of Fig. 4 only those of the ζ-curve represent stable states. Of all chords which we may imagine to be drawn in Fig. 5, one, $a'b'$, touches the ζ-curve in two points. The part $a'e'b'$ of the ζ-curve lies above this chord $a'b'$. If we now imagine vertical lines drawn through the points between W and a, between a and b, and between b and X, we see that of all conceivable ζ-points of Fig. 5 only those of the parts $W'a'$ and $b'X'$ of the ζ-curve and those of the double tangent $a'b'$ represent stable states. This means that only the liquids of Wa and bX and the system $L(a) + L(b)$ are stable.

8. We now assume that the points of WX represent mixed crystals. Then their ζ-curve may also have the form shown in Fig. 4 or Fig. 5. When Fig. 4 obtains, it follows that the two solid components W and X are miscible with each other in all proportions and form an unbroken series of mixed crystals. When Fig. 5 obtains, then only the mixed crystals of Wa and bX are stable; all others (namely between a and b) are metastable or unstable, and separate or tend to separate into the stable system $M(a) + M(b)$, i.e., into a mixture of the mixed crystals $M(a)$ and $M(b)$. In this case no continuous series of mixed crystals exists and consequently the two solid components W and X are not miscible with each other in all proportions.

9. Since vapors (gases) are miscible with one another in all proportions their ζ-curve always has the form shown in Fig. 4.

10. If we represent the entropy and volume of a phase by η and v respectively, then we have in accordance with Gibbs the following relations:

$$d(\zeta)_p = -\eta dt, \qquad d(\zeta)_t = vdp, \tag{9}$$

for $d\epsilon = td\eta - pdv$, and differentiation of $\zeta = \epsilon - t\eta + pv$ gives

$$d\zeta = d\epsilon - td\eta - \eta dt + pdv + vdp,$$

whence

$$d\zeta = vdp - \eta dt.$$

This means that the ζ of a phase decreases when the temperature (at constant pressure) increases, and increases when the pressure (at constant temperature) increases.* If we apply this to every point of a ζ-curve in our diagrams we see that every point of a ζ-curve sinks towards the x-axis with increase of t. As, however, all phases do not possess the same entropy and consequently all ζ-points do not sink at the same rate, it follows that *with increase of temperature the ζ-curve sinks, with decrease of temperature it rises, its form changing at the same time.* If we represent the ζ-points of solid W and solid X by (W) and (X) respectively, then they also will sink with rise of temperature and rise with fall of temperature. Since the liquids W and X have greater entropies (at a given temperature) than the corresponding solid substances W and X, the points W' and X' sink with rise of temperature and rise with fall of temperature, but in each case at a faster rate than the corresponding points (W) and (X).

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* When the phases are closed and the components independent, $\Sigma \mu dm = 0$.

III. Binary Systems in Which Besides Liquids Only the Solid Components W and X Can Occur

11. In a system formed from the components W and X, liquids, vapors and solid substances may occur, viz.: the pure substances W and X and their compounds or mixed crystals. It depends on the values of t and p, and on the nature of the components, which of these phases are formed. At first we take a system in which neither compounds nor mixed crystals occur. If now we make the pressure so high that no vapor can be formed, then the only types of phases possible will be liquids and solids W and X. We have therefore only to deal with the ζ-curve and the points (W) and (X). Furthermore, we shall assume in the first place that the ζ-curve is wholly convex towards the composition axis (Fig. 4, Figs. 6–9).

If we lower the temperature for which Fig. 4 obtains, then, as we have seen, the points (W) and (X) and the whole ζ-curve will rise. Since X' rises more rapidly than (X), these points will first become coincident, after which X' will rise above (X). When this is the case, but W' is still below (W), we get Fig. 6. With further fall of temperature W' also rises above (W) and we get Fig. 7. Thus with continued decrease of temperature we have the succession of diagrams: Fig. 4—Fig. 6—Fig. 7—Fig. 8—Fig. 9.

We now represent the melting-points* of solids W and X (under a definite pressure) by $T(W)$ and $T(X)$, and for the sake of definiteness we take $T(X) > T(W)$, e.g., X = a salt and W = water. We call the T for which Fig. 8 holds good $T(e)$. Later on we shall see that this is the eutectic temperature of the system. We can now distinguish the following cases for the temperature T:

(i) $T > T(X) > T(W) > T(e)$. As T now is higher than the melting-points of each of the components X and W, these are stable only in the liquid state and hence W' is lower than (W), X' lower than (X), (case of Fig. 4).

(ii) $T(X) > T > T(W) > T(e)$. The stable state of X is the solid state, hence (X) is lower than X'. The point W' is, however, still below (W) (case of Fig. 6).

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*From this point onwards in the present article, and in the corresponding figures, temperature is denoted by T.

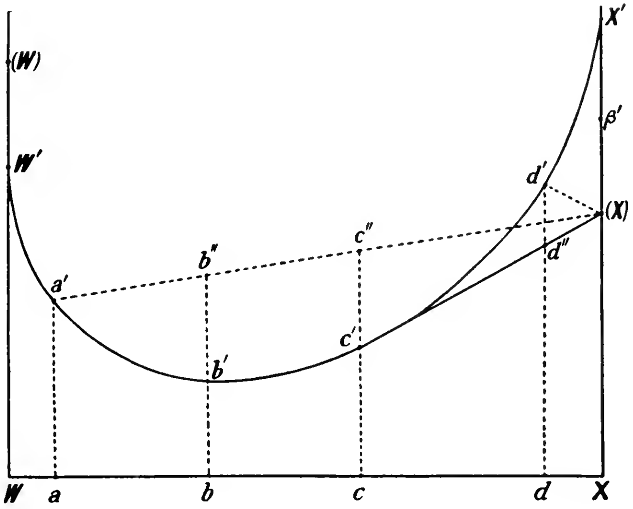

FIG. 6

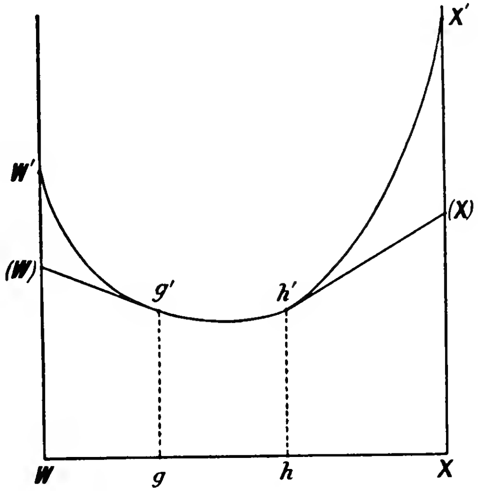

FIG. 7

(iii) $T(X) > T(W) > T > T(e)$. Since now, by similar reasoning, (X) lies below X' and (W) below W', we have one of the Figs. 7, 8, and 9. As we take $T' > T(e)$, we get the case of Fig. 7.

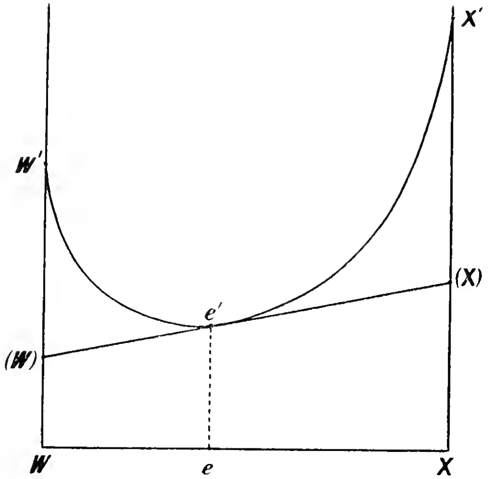

FIG. 8

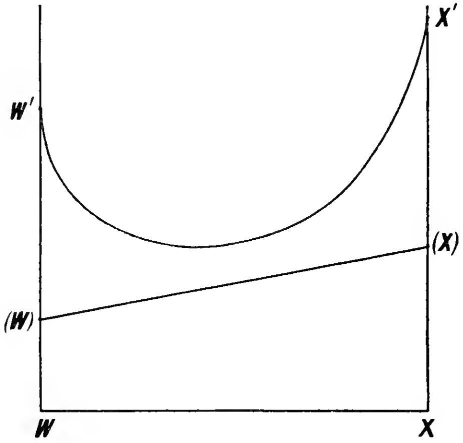

FIG. 9

(iv) $T(X) > T(W) > T = T(e)$ (case of Fig. 8).
(v) $T(X) > T(W) > T(e) > T$ (case of Fig. 9).

12. We shall now deduce which phases and systems (phase-complexes) are stable in each of these five cases. We shall represent them in Fig. 10, in which temperature has been taken as the ordinate (isobaric T-x diagram). The points $T(W)$ and $T(X)$ in this figure represent the respective melting-points of the substances W and X.

(i) $T > T(X) > T(W) > T(e)$ (Fig. 4). We have already seen that in this case the stable states for W and X are the liquid state, and that all liquids are stable. We represent these liquids in Fig. 10 by the points of a line 1.1′ situated above $T(X)$.

(ii) $T(X) > T > T(W) > T(e)$ (Fig. 6). Every straight line uniting an arbitrary point z' of the ζ-curve with the point (X) is the ζ-line of a system

$$L(z) + \text{solid } X, \tag{10}$$

consisting of the two phases, liquid z and solid X. If we take, for example, the line $a'(X)$, then every point of this line (e.g., b'', c'', etc.) represents the ζ-point of a system, $L(a)$ + solid X. Similarly every point of the line $c'(X)$ represents the ζ-point of a system $L(c)$ + solid X. So we may imagine an infinite number of lines $z'(X)$, of which in Fig. 6 only $a'(X)$, $c'(X)$ and $d'(X)$ have been drawn. Of all these conceivable lines, the line $c'(X)$, touching the ζ-curve in c', plays a great part. It is clear from the diagram that the ζ-points of all phase-complexes whose compositions lie between W and c lie above the corresponding points of the ζ-curve (ζ-points of the liquids of corresponding composition), whilst the ζ-points of all liquids whose compositions lie between c and X lie *above* the corresponding ζ-points of the phase-complex $L(c)$ + solid X. Hence of all conceivable ζ-points of Fig. 6 only those of the part $W'a'b'c'$ of the ζ-curve and those of the tangent $c'(X)$ represent stable states. Thus of all conceivable systems of the type (10) only the system

$$L(c) + \text{solid } X \tag{11}$$

is stable. *Thus $L(c)$ represents the liquid saturated with respect to solid X and therefore in equilibrium with it.* All liquids between c and X are supersaturated and tend to pass into (11) with separation of solid X, whilst all liquids between W and c

are unsaturated. If we imagine the liquid c represented by point c in Fig. 10, then the points of $2 \cdot c$ represent unsaturated liquids, whilst the points of $c \cdot 2'$ represent supersaturated liquids which pass into the system (11).

(iii) $T(X) > T(W) > T > T(e)$ (case of Fig. 7). Since

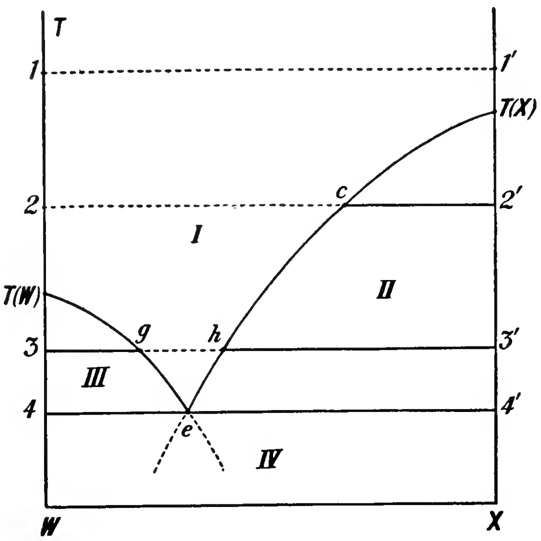

FIG. 10

both the substances W and X are now solid we may imagine the systems

$$\left.\begin{array}{c} L(u) + \text{solid } W, \qquad L(z) + \text{solid } X, \\ \text{solid } W + \text{solid } X. \end{array}\right\} \qquad (12)$$

Besides the lines $z'(X)$ discussed above, we must now imagine in Fig. 7 also the lines $u'(W)$ and $(W)(X)$, and we can now draw a tangent to the ζ-curve through each of the points (W) and (X). If g' and h' are the respective points of contact, we see that of all conceivable ζ-points of Fig. 7 only those of the tangents $(W)g'$ and $h'(X)$, and those of the part $g'h'$ of the ζ-curve, represent stable states. From this it follows that of all conceivable systems (12), only $L(g)$ + solid W and $L(h)$ + solid X are stable.

Liquid g is saturated with respect to solid W, and liquid h with respect to solid X. All liquids between W and g are supersaturated with respect to solid W, all liquids between h and X with respect to solid X. All liquids between g and h are unsaturated. In Fig. 10 the liquids g and h are represented by the points g and h of the line 3.3′.

(iv) $T(X) > T(W) > T = T(e)$ (case of Fig. 8). When the points of contact g' and h' of Fig. 7 coincide we obtain Fig. 8, in which the ζ-curve and the straight line $(W)(X)$ touch one another in the point e'. In this case we see that of all conceivable ζ-points of Fig. 8 only those of the line $(W)e'(X)$ represent stable states. Since the point e' lies not only on this straight line but also on the ζ-curve, the point e' may now represent not only solid W + solid X but also the liquid of composition e. We now have a ζ-line of which not only the two end points but also a third point e' represent stable phases. Every point of the line $(W)(X)$ can represent therefore a system solid W + solid X, whilst each point of the part $(W)e'$ can represent also a system $L(e)$ + solid W, and each point of the part $e'(X)$ also a system $L(e)$ + solid X. From this it follows that of all liquids only the liquid e is now stable, whilst of all conceivable systems (12) only the systems:

$$\left.\begin{array}{cc} L(e) + \text{solid } W, & L(e) + \text{solid } X, \\ \multicolumn{2}{c}{\text{solid } W + \text{solid } X,} \end{array}\right\} \tag{13}$$

are stable. Since $L(e)$ is saturated with respect both to W and X, therefore also the three-phase system

$$L(e) + \text{solid } W + \text{solid } X \tag{14}$$

can exist, in which the reaction

$$\text{solid } W + \text{solid } X \rightleftarrows L(e) \tag{15}$$

can occur. For we have already seen that the liquid e has the same ζ as a system, solid W + solid X, with the composition e

(i.e., $\zeta = ee'$). The ζ of the three-phase system (14) remains unchanged, therefore, whether the reaction (15) occurs in the one or the other direction. When this reaction proceeds from left to right, heat is absorbed; when it proceeds from right to left, heat is produced. Given a unit system of composition e at temperature $T(e)$ (and the given pressure) we cannot predict its *phase structure* without further information (e.g., concerning its past history, or its behavior on adding or abstracting heat energy, etc.).

The liquid e is represented in Fig. 10 by the point e, and the systems discussed by points on the line $4 \cdot e \cdot 4'$.

(v) $T(X) > T(W) > T(e) > T$ (case of Fig. 9). Since the line $(W)(X)$ now lies wholly below the ζ-curve (the free energy *liquidus* curve), all the liquids are metastable and tend to pass into the mixture, solid W + solid X. From this discussion it follows that $T(e)$ is the lowest temperature for the existence of a stable liquid phase. $T(e)$ is therefore the *eutectic* temperature and $L(e)$ the *eutectic* liquid of the (W, X) system. If we take W = water, so that the three-phase system (14) becomes $L(e)$ + ice + solid X, then we call $T(e)$ also the *cryohydrate* temperature.

13. From the preceding considerations we can now make the following statements about Fig. 10. The liquids saturated with solid W are represented by the points of a curve $eT(W)$, the saturation curve of W, whilst the liquids saturated with solid X are represented by the points of a curve $eT(X)$, the saturation curve of X. These two curves and the line $4 \cdot e \cdot 4'$ divide Fig. 10 into four fields. Each point of field I represents an unsaturated liquid. Each point of field II represents a system $L(z)$ + solid X, or alternatively a liquid which is supersaturated with respect to solid X. Similarly each point of field III represents a system $L(u)$ + solid W, or a liquid supersaturated with respect to solid W, whilst finally each point of field IV represents a mixture of solid W and solid X.

The two saturation curves do not terminate in e but are prolonged into field IV, in which they represent metastable states. We find the points of these prolongations, and we see also that they represent metastable states, when we imagine tangents to the ζ-curve drawn from the points (W) and (X) of Fig. 9 (and similar figures).

14. When the solid substance X can exist in the two modifications α and β, we may suppose the ζ-point of solid α in Fig. 6 represented by (X) and that of solid β by β', so that the modification β is metastable with respect to α. If we draw a tangent to the ζ-curve from β', the point of contact, which is situated somewhere between c' and X', represents the ζ-point of the liquid saturated with respect to solid β, whilst the liquid itself lies somewhere between c and X. From this it follows that, when a substance X exists in two or more modifications, the most stable form has the smallest solubility.

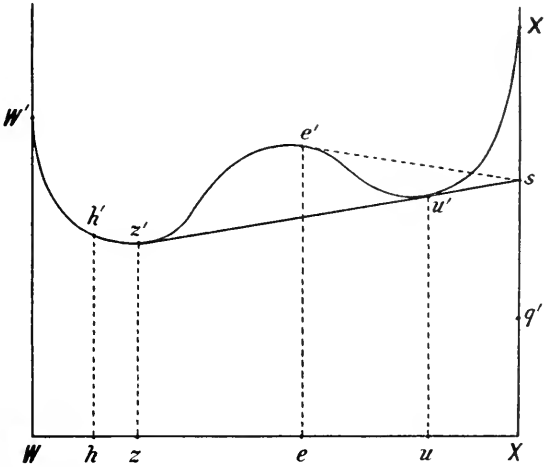

FIG. 11

15. In Fig. 11, in which the ζ-curve has a part concave to the composition axis, the point of intersection of the double tangent $z'u'$ with the line XX' has been represented by the point s. If we take $T = T(X)$, then (X), i.e., the ζ-point of solid X, coincides with X'. If we lower the temperature, then the point (X) and the ζ-curve rise, whilst the latter also changes its form. Since, however, X' rises more rapidly than (X), the point (X) comes to fall below X', and the lower the temperature the lower it becomes. Hence the point (X) lies at first between X' and s; then it coincides with s at a definite temperature, which we shall call $T(s)$, and afterwards it lies below s. If we leave out of consideration the occurrence of solid W, we may now distinguish the following three cases.

(i) $T(X) > T > T(s)$. We imagine the point (X), which is now situated between X' and s, represented by p' in Fig. 5. If we now draw the tangent $p'd'$, we see that of all conceivable ζ-points of Fig. 5, only those of the parts $W'a'$ and $b'd'$ of the ζ-curve and those of the lines $a'b'$ and $d'p'$ represent stable states. From this follows: all liquids of Wa and bd (Fig. 5) are stable; all liquids between a and b separate into the system $L(a) + L(b)$; all liquids between d and X are supersaturated and pass into the system $L(d)$ + solid X. Consequently, of all conceivable systems, only $L(a) + L(b)$ and $L(d)$ + solid X can occur in a stable state. We imagine these liquids a, b, and d represented by the points a, b and d of the line 1.1′ in Fig. 12.

(ii) $T(X) > T = T(s)$. Now we imagine the point (X) at the point s of Fig. 11. We see that, of all conceivable ζ-points of Fig. 11, only those of the part $W'z'$ of the ζ-curve and those of the line $z'u's$ represent stable states. This line $z'u's$, just like the line $(W)e'(X)$ of Fig. 8, has a special property, namely that not two but three of its points represent stable phases, i.e., z' and u' represent the liquids z and u, and s the solid substance X. From this follows: of all liquids, only those of Wz and the liquid u are stable (Fig. 11). Of all conceivable systems, only

$$L(z) + \text{solid } X, \qquad L(u) + \text{solid } X, \qquad L(z) + L(u), \tag{16}$$

and the three-phase system

$$L(z) + L(u) + \text{solid } X \tag{17}$$

are stable. We see that *two* liquids now exist, namely z and u, both of which are saturated with respect to solid X.

In the same way that we deduced reaction (15) for the three-phase system (14) of Fig. 8, we now find that in the three-phase system (17) the reaction

$$L(z) + \text{solid } X \rightleftarrows L(u) \tag{18}$$

can occur. On addition of heat $L(z)$ passes into $L(u)$ with solution of solid X, whilst on removal of heat $L(u)$ breaks up into $L(z)$ and solid X. If in Fig. 12 we represent the liquids z and u by the points z and u, then the systems discussed above are all represented by the points of the portion $zu2'$ of the line $2.2'$.

(iii) $T(X) > T(s) > T$. The point (X) must now be situated below the point s. Although the ζ-curve has now a somewhat different form and is also situated higher than in Fig. 11, nevertheless we may imagine it as represented in this figure, and call the latter now Fig. 11*a*. We suppose the point (X) to be at q'. Imagine a line through q' touching the ζ-curve in a point h' between W' and z'. It is then clear that of all conceivable ζ-points of Fig. 11*a* only those of the part $W'h'$ of the ζ-curve and those of the tangent $h'q'$ represent stable states. From this follows for Fig. 11*a*: all liquids of Wh are stable, whilst all other liquids, i.e., those of hX, pass into the system

$$L(h) + \text{solid } X \tag{19}$$

with separation of solid X. If in Fig. 11 we imagine z' and u' substituted by m' and n', we see that the system

$$L(m) + L(n) \tag{20}$$

also exists, but only in a metastable state. When the stable state is attained, these two liquids disappear, with formation of the system (19). In Fig. 12 the liquids h, m and n, are represented by points of the line $3.3'$.

When we raise the temperature, the ζ-curve not only shifts downwards but also changes its form. As the points of contact a' and b' in Fig. 5 are moved with respect to one another the liquids a and b also change their composition. When a' and b' coincide in a point c' at a definite temperature $T(c)$, the liquids become identical in composition. We call c a *critical* liquid and

$T(c)$ a *critical solution temperature.* This temperature may be higher or lower than $T(X)$.

16. The line $zu2'$ and the curves hz, zcu and $uT(X)$ divide Fig. 12 into fields, the meaning of which follows from the preceding considerations. At the same time it is apparent that the field zcu, i.e., the heterogeneous two-liquid phase field, does not end at the line zu but extends farther downwards, although in a metastable condition. As the liquids saturated with respect to X are represented by the curves hz and $uT(X)$, the solubility of X at $T(s)$ does not change continuously but jumps from z to u. If, however, we also consider metastable and unstable states, then a continuous transition from z to u exists. The saturation curve of X consists, as we shall presently show, of a curve $hzgekuT(X)$ having a maximum temperature in g and a minimum temperature in k.

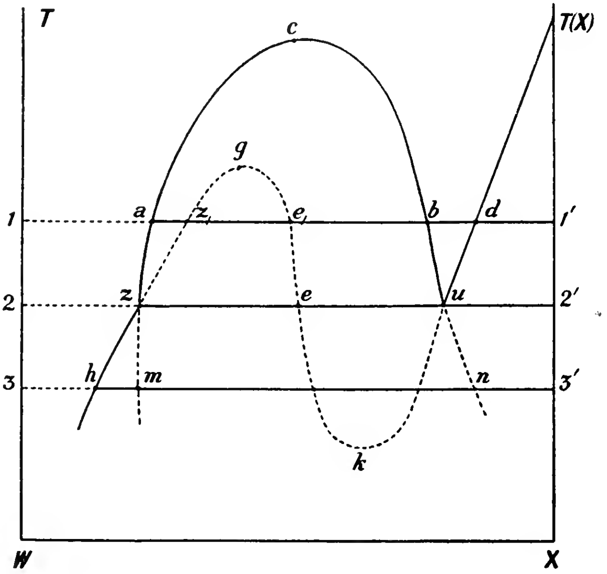

FIG. 12

In order to prove this, we at first imagine $T = T(s)$, so that (X) in Fig. 11 coincides with s. Besides the two coincident tangents $z'(X)$ and $u'(X)$ we may also draw a third tangent $e'(X)$. Consequently, besides the liquids z and u there exists also a third liquid e which is saturated with respect to X. So in Fig. 12 there is possible, between z and u, a liquid e saturated with respect to X which is not stable (as appears from Fig. 11). We now take a temperature somewhat higher than $T(s)$, so that (X) in Fig. 11 is situated a little above s. We may now draw three tangents through (X), which we shall call $z_1'(X)$, $e_1'(X)$ and $u_1'(X)$. Then point z_1' is situated a little to the right of z', e_1' a little to the left of e' and u_1' a little to the right of u'. Of the three liquids saturated with respect to X, which we call z_1, e_1 and u_1, now only u_1 is stable, as appears from Fig. 11. In Fig. 12 we represent them by the points z_1, e_1 and d (i.e., $d = u_1$). If we raise the temperature still higher, then, as follows from Fig. 11, the points z_1 and e_1 of Fig. 12 coincide finally in a point g. In a corresponding manner we may prove that in Fig. 12 there exists also the metastable-unstable branch eku. From this it appears that the saturation curve of X is a continuous curve with a maximum and a minimum temperature. Only the parts hz and $uT(X)$ which lie outside the heterogeneous two-liquid field represent stable liquids. The other liquids are metastable (viz., zg and ku) or unstable (viz., gk).

IV. Binary Systems in Which Besides Liquids Only the Solid Components *W* and *X* and a Solid Compound May Occur.

17. When W and X form a compound H, we may imagine the systems:

$$\text{solid } W + \text{solid } X, \tag{21}$$

$$\text{solid } W + \text{solid } H, \qquad \text{solid } X + \text{solid } H, \tag{22}$$

$$\text{solid } W + \text{solid } X + \text{solid } H, \tag{23}$$

when we leave liquid phases out of account. The compound and its ζ-point are represented by H and (H) in Figs. 13, 14, and 16. If in Fig. 14 we imagine the curves omitted and consider only the ζ-points (W), (H) and (X), together with their conjugation lines, we may distinguish three cases.

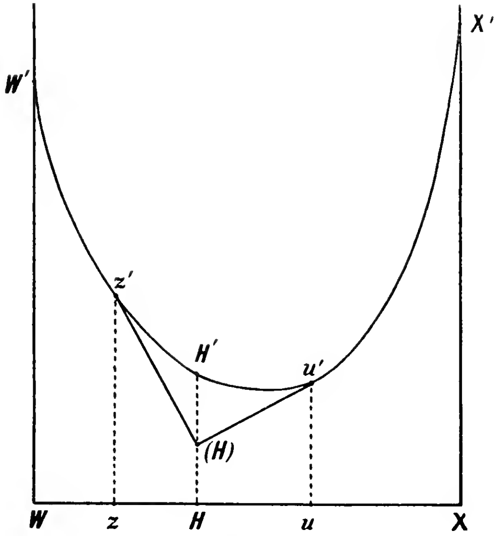
X'
W'
z'
H'
u'
(H)
W
z
H
u
X

FIG. 13

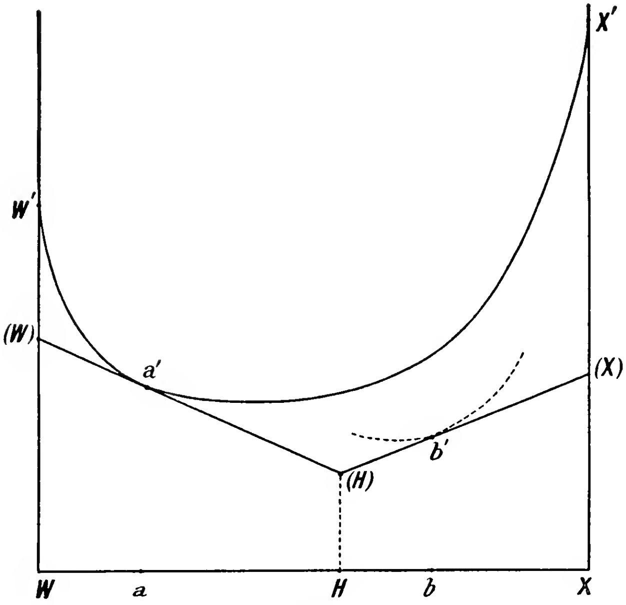
X'
W'
(W)
a'
(X)
b'
(H)
W
a
H
b
X

FIG. 14

(i) Point (H) is situated below $(W)(X)$ (as in Fig. 14). It is clear that only the points of $(W)(H)$ and of $(H)(X)$ represent stable states, so that both the systems (22) are stable whilst (21) is metastable. From this it follows that the solid substances W and X cannot exist next to each other in stable equilibrium, and that the reaction

$$\text{solid } W + \text{solid } X \rightarrow \text{solid } H \tag{24}$$

will tend to occur.

(ii) Point (H) is situated above $(W)(X)$. It is clear that now only the points of $(W)(X)$ represent stable states; in other words, system (21) is stable, whilst both the systems (22) are metastable. Thus the compound H is now metastable and tends to separate into its components according to the reaction

$$\text{solid } W + \text{solid } X \leftarrow \text{solid } H. \tag{25}$$

(iii) Point (H) is situated on the line $(W)(X)$. We have now again the special case that three points of a line represent stable phases (compare also $(W)e'(X)$ in Fig. 8 and $z'u's$ in Fig. 11). It is clear that all the systems (21), (22) and (23) are now stable and that the reaction

$$\text{solid } W + \text{solid } X \rightleftarrows \text{solid } H \tag{26}$$

can occur. The direction of the reaction on addition of heat will depend on whether the compound is endothermic or exothermic. It depends on the temperature and the pressure which of the three cases mentioned above will occur. In the considerations that follow we shall suppose that (H) always lies below $(W)(X)$.

18. In Fig. 13 the point H' of the ζ-curve is the ζ-point of a liquid which has the same composition as the solid compound, i.e., H' is the ζ-point of liquid H. Denoting the melting-point of H (under the pressure p) by $T(H)$, then $T < T(H)$. If we draw the two tangents $z'(H)$ and $u'(H)$ we see that they represent more stable systems than the points on the part $z'H'u'$ of the ζ-curve. From this follows: liquids between z and u (Fig. 13) are supersaturated; those between z and H separate into

$L(z)$ + solid H, those between u and H into $L(u)$ + solid H, whilst liquid H solidifies to solid H. Thus two liquids, z and u, exist, both saturated with respect to solid H; z has a smaller, u a greater amount of X than the compound. In Fig. 15 these liquids are represented by the points z and u. As (H) and H' approach one another with increase of temperature and finally coincide at $T = T(H)$, so also z' and u' coincide at this temperature. Consequently the saturation curve of H will have the shape amq, shown in Figs. 15 and 17, with a temperature maximum at $T(H)$, shown at point m.

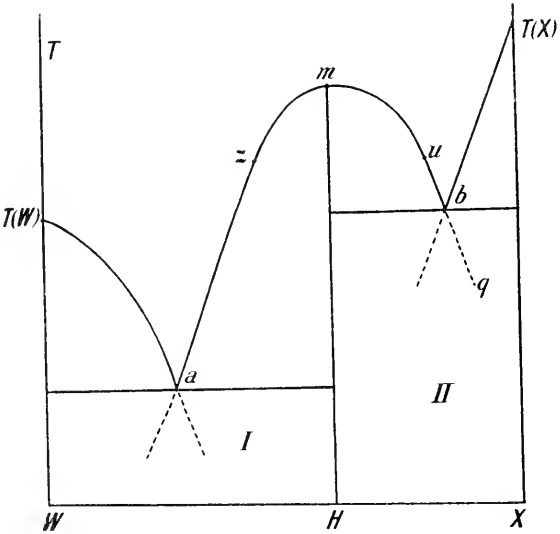

FIG. 15

We now imagine the ζ-curve of Figs. 14 and 16 at first totally above the lines $(W)(H)$ and $(H)(X)$. Since with increase of temperature the ζ-curve approaches the composition axis WX more rapidly than these lines, it will lie totally *below* them at a sufficiently high temperature. Consequently the ζ-curve will touch the line $(W)(H)$ in a point a' at a definite temperature $T(a)$, and will touch the line $(H)(X)$ in a point b' at a definite temperature $T(b)$. If we take $T(a) < T(b)$, then a' lies between (W) and (H); the point b', however, may then be situated as in Fig. 14 or as in Fig. 16. We shall now deduce that the equilibria resulting from Fig. 14 may be represented by Fig. 15, and those resulting from Fig. 16 by Fig. 17.

19. At $T = T(a)$ three points of the line $(W)a'(H)$ of Fig. 14 represent stable phases. So at $T = T(a)$ the reaction

$$\text{solid } X + \text{solid } H \rightleftarrows L(a) \qquad (27)$$

can occur. We represent $L(a)$ in Fig. 15 by the point a. At a temperature a little higher than $T(a)$ the ζ-curve intersects the line $(W)(H)$; we may now draw tangents from (W) and (H), the points of contact representing liquids saturated with respect to W and H respectively. At a temperature a little lower than $T(a)$ the ζ-curve lies above $(W)(H)$, so that only solid W and solid H exist as stable states. The tangents drawn from (W) and (H) now represent metastable systems only. From Fig. 14 we may therefore make the following deductions regarding Fig. 15. A field, solid W + solid H, must be situated below point a (Field I); two saturation curves, namely those of W and H, must run through the point a, their parts proceeding towards higher temperatures representing stable liquids, whilst the parts situated in Field I represent metastable liquids. In a corresponding manner it is apparent that at $T = T(b)$ the reaction

$$\text{solid } H + \text{solid } X \rightleftarrows L(b) \qquad (28)$$

can occur. If in Fig. 15 we represent $L(b)$ by point b, we find that the saturation curves running through b must be situated as shown, whilst Field II represents solid H + solid X.

Since we have already proved that the saturation curve of H must have a maximum at $T = T(H)$ in point m, it follows that we can represent by Fig. 15 all the equilibria resulting from Fig. 14.

20. At $T = T(a)$ in Fig. 16 the same obtains for the line $(W)a'(H)$ as in Fig. 14. At $T = T(b)$, however, in Fig. 16 the point (H) is situated between b' and (X). Instead of reaction (28) we must now have

$$\text{solid } H \rightleftarrows L(b) + \text{solid } X. \qquad (29)$$

If we represent, in Fig. 17, $L(b)$ by b, then this point must now lie to the left of line Hm and not to the right, as in Fig. 15.

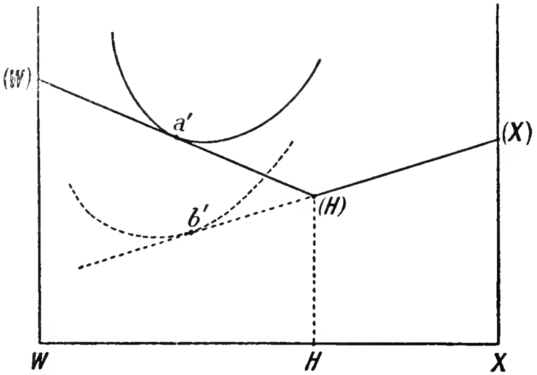

FIG. 16

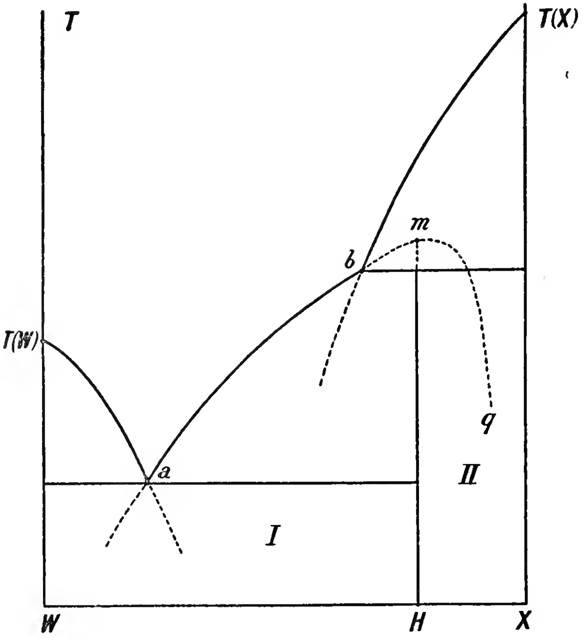
T
T(X)
m
b
T(W)
q
a
II
I
W
H
X

FIG. 17

At a temperature a little higher than $T(b)$ the ζ-curve intersects the line $(H)(X)$ (Fig. 18). We may now draw the lines $h'(H)$ and $x'(X)$ which touch the ζ-curve in the points h' and x' (not shown). Hence point h' is the ζ-point of a liquid h, saturated with respect to H and x' that of a liquid saturated with respect to X. Thus at this temperature the systems

$$L(h) + \text{solid } H, \qquad L(x) + \text{solid } X, \tag{30}$$

exist. It appears from the position of these points of contact in Fig. 18 that $h'(H)$ and $(H)(X)$ are situated above $x'(X)$. Therefore the first one of the systems (30) is metastable, the second one stable. From this it follows that at $T > T(b)$ the saturation curve of H is metastable, that of X stable.

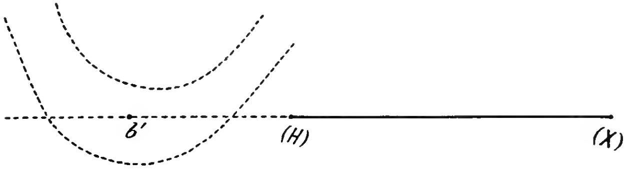

Fig. 18

If we take $T < T(b)$, the ζ-curve lies above $(H)(X)$ (Fig. 18). If we now also imagine the tangents $h'(H)$ and $x'(X)$ drawn, then we see that $h'(H)$ and $(H)(X)$ now lie below $x'(X)$. From this follows: at $T < T(b)$ the saturation curve of H is stable, but that of X metastable; also solid H + solid X (Field II) is a stable system. We can now make the following deductions from Fig. 16 as regards Fig. 17. Two saturation curves, namely those of H and X, must go through point b of Fig. 17. Towards higher temperatures that of H is metastable and that of X stable, whilst towards lower temperatures the reverse holds good.

In Fig. 15, at $T = T(b)$, reaction (28) occurs, so that $T(b)$ is the common melting point or the eutectic temperature of H and X. In Fig. 17, at $T = T(b)$ reaction (29) occurs. Then $T(b)$ is, as appears also from Fig. 17, the highest temperature at which solid H can exist, or the temperature at which solid H decomposes with formation of a liquid and separation of solid X.

V. Note by F. G. Donnan. (Analytical Addendum to the Geometry)

It can be proved in the following manner that the ζ-curve touches the lines WW' and XX' at the points W' and X' respectively (see page 296 of Professor Schreinemakers' article). Denoting by ζ_n the zeta function (free energy) for a liquid phase containing n_1 mols of X and n_2 mols of W, where $n_1 + n_2 = n$, then it follows from Euler's theorem that

$$\zeta_n = n_1 \left(\frac{\partial \zeta_n}{\partial n_1}\right)_{n_2,\, p,\, t} + n_2 \left(\frac{\partial \zeta_n}{\partial n_2}\right)_{n_1,\, p,\, t},$$

since ζ_n is a homogeneous function of the first degree in n_1 and n_2. This expression may be written in the convenient form $\zeta_n = n_1\bar{\zeta}_1 + n_2\bar{\zeta}_2$, when $\bar{\zeta}_1$ and $\bar{\zeta}_2$ are termed the *partial molar free energies* of X and W respectively. Since $\bar{\zeta}_1 = \mu_1$, $\bar{\zeta}_2 = \mu_2$, we shall follow the notation of Gibbs and write $\zeta_n = n_1\mu_1 + n_2\mu_2$, where μ_1 and μ_2 are the *potentials* (per mol) of the components X and W respectively. For unit (molar) phase we must divide by $n_1 + n_2$, and write therefore

$$\frac{\zeta_n}{n_1 + n_2} = \zeta = x\mu_1 + (1 - x)\,\mu_2,$$

where

$$x = \frac{n_1}{n_1 + n_2}, \qquad 1 - x = \frac{n_2}{n_1 + n_2}.$$

This expresses the ζ of unit phase in terms of the composition parameter x and the potentials. At constant temperature and pressure μ_1 and μ_2 are functions of x only.

Differentiating the expression $\zeta_n = n_1\mu_1 + n_2\mu_2$ for a change of n_1 and n_2 at constant temperature and pressure (change of composition),

$$d\zeta_n = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2.$$

But

$$d\zeta_n = \mu_1 dn_1 + \mu_2 dn_2$$

under like conditions. Hence,

$$n_1\,d\mu_1 + n_2\,d\mu_2 = 0, \quad \text{or} \quad x\frac{d\mu_1}{dx} + (1 - x)\frac{d\mu_2}{dx} = 0.$$

Differentiation of $\zeta = x\mu_1 + (1 - x)\mu_2$ with respect to x (at constant temperature and pressure) gives

$$\frac{d\zeta}{dx} = x\frac{d\mu_1}{dx} + \mu_1 + (1 - x)\frac{d\mu_2}{dx} - \mu_2 = \mu_1 - \mu_2,$$

from the preceding result. Thus at any x-point of the ζ-curve, we can determine both μ_1 and μ_2 by means of the two equations

$$\zeta = x\mu_1 + (1 - x)\,\mu_2,$$

$$\frac{d\zeta}{dx} = \mu_1 - \mu_2,$$

whence we deduce the results

$$\mu_1 = \bar{\zeta}_1 = \zeta + (1 - x)\frac{d\zeta}{dx},$$

$$\mu_2 = \bar{\zeta}_2 = \zeta - x\frac{d\zeta}{dx}.$$

Consider now the state of affairs for $x = 0$ (pure W). From the preceding results we have

$$(\mu_1)_{x=0} = (\zeta)_{x=0} + \left(\frac{d\zeta}{dx}\right)_{x=0}.$$

It is clear that $(\zeta)_{x=0}$ is the ζ (free energy) of 1 mol of pure W. Now μ_1 is the increase of free energy of an infinite phase of composition x on the addition (at constant pressure and temperature) of one mol of X, whilst $(\mu_1)_{x=0}$ is the limiting value to which μ_1 approaches as x approaches zero.

Let p_1 denote the partial vapor pressure of X in equilibrium with the liquid phase of composition x at the given pressure and temperature, and let $(p_1)_0$ denote the vapor pressure of X in equilibrium with pure liquid X at the same temperature and pressure. Also let $(\mu_1)_0$ denote the free energy (potential) of 1 mol of pure liquid X under the same conditions. Then $(\mu_1)_0 - \mu_1 =$ total diminution of free energy resulting from the transference of 1 mol of X from the pure liquid state (as above defined) to an infinite mass of liquid of composition x (as above defined). It is easy to show that $(\mu_1)_0 - \mu_1 = \int_{p_1}^{(p_1)_0} vdp$, where $v =$ volume of one mol of the vapor of X at the given temperature. Now v is a function of p, and for $x = 0$, $p_1 = 0$, and $v = +\infty$. Hence when $x = 0$ the value of $\int_{p_1}^{(p_1)_0} vdp$ becomes $+\infty$, so that $(\mu_1)_{x=0} = -\infty$. From the preceding results it follows therefore that $\left(\frac{d\zeta}{dx}\right)_{x=0} = -\infty$. Hence the ζ-curve touches the line WW' at the point W'. Similarly the ζ-curve touches the line XX' at the point X'.

From the preceding analysis it is also evident that at the minimum point of the ζ-curve, $\mu_1 = \mu_2 = (\zeta)_{\text{min}}$.

An analytical and a graphical treatment of solid-liquid phase equilibria in binary systems was given by A. C. van Rijn van Alkemade (*Verhand. Akad. Wetensch. Amsterdam*, **1**, 1 Sec., No. 5, (1892); *Zeitsch. f. physikal. Chemie*, **11**, 289 (1893)), who based his discussion on the properties of Gibbs' ζ-function. In his graphical treatment van Alkemade employed a *ratio* instead of a *fractional* composition parameter, so that the part of the diagram referring to one pure component is situated at infinity. The method employed by Schreinemakers avoids this defect, and is therefore much more general.

It may be remarked in conclusion that the preceding analysis establishes very simply the geometrical method for determining the point on the ζ-curve which corresponds to a liquid in equilibrium with a pure solid phase, say pure solid W, for example. Let $P_1(\zeta_1, x_1)$ and $P_2(\zeta_2, x_2)$ be two points on the ζ-curve. The equation of the straight line P_1P_2 is

$$\frac{\zeta_2 - \zeta}{x_2 - x} = \frac{\zeta_2 - \zeta_1}{x_2 - x_1}.$$

Suppose this line cuts the WW' axis in the point $P_0(\zeta_0,0)$. Then

$$\frac{\zeta_2 - \zeta_0}{x_2} = \frac{\zeta_2 - \zeta_1}{x_2 - x_1}.$$

Allow the points P_1 and P_2 to coalesce in the tangent point $Q_m(\zeta_m, x_m)$, the tangent line passing through P_0. Then we get

$$\frac{\zeta_m - \zeta_0}{x_m} = \left(\frac{d\zeta}{dx}\right)_{x = x_m},$$

or

$$\zeta_0 = \zeta_m - x_m\left(\frac{d\zeta}{dx}\right)_{x = x_m} = (\mu_2)_{x = x_m}.$$

This result shows that the pure solid phase corresponding to the point P_0 on WW' is in equilibrium with the liquid x_m determined by the tangent from P_0 to the ζ-curve. It is to be observed that P_0 is (W) in the notation of Schreinemakers.

I

THE CONDITIONS OF EQUILIBRIUM FOR HETEROGENEOUS MASSES UNDER THE INFLUENCE OF GRAVITY AND OF CENTRIFUGAL FORCE

[*Gibbs, I, pp. 144–150*]

DONALD H. ANDREWS

THE effect of gravity on the equilibrium of fluids has interested physicists and chemists for many hundreds of years. A list of those who have contributed observation and theory to this field includes many famous names such as Galileo, Laplace and Boltzmann. It is Gibbs' characteristic rôle to have shown how these special relations of gravity and fluid equilibrium fit into the general scheme of thermodynamics in a way that permits of the widest sort of application.

Little comment is needed on the actual derivation of the equations.* The usual thermodynamic system is postulated, including in this case the force of gravity. The laws of thermodynamics and the various equations of condition then lead to the equations which define the state of the system.

Temperature must be constant throughout, i.e.,

$$t = \text{const.}; \qquad [228]$$

and the pressure must vary with the height,i.e.,

$$dp = -g\gamma dh. \qquad [233]$$

The chemical potentials ($\mu_1, \ldots \mu_m$) of the individual components (essentially the partial pressures if the system is not far from ideal) must satisfy the equations

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*Compare Section XIII of Article L of this volume.

$$\left.\begin{array}{l}\mu_1 + gh = \text{const.}\\ \cdots\cdots\cdots\cdots\cdots\\ \mu_m + gh = \text{const.}\end{array}\right\} \qquad [234]$$

It is emphasized in the text that we must distinguish the $\mu_1, \ldots \mu_m$, *intrinsic* potentials, from the general potentials of the components which include the action of gravity and are analogous to the partial molal free energies. These latter are of course constant throughout the system.

In the second part of this section (Gibbs, I, 147–150), *Method of treating the preceding problem, in which the elements of volume are regarded as fixed,* more detailed attention is given to the factors introduced by the discontinuities between phases in a system under the influence of gravity. The condition of equilibrium is found to be that "the pressure at any point must be as great as that of any phase of the same components for which the temperature and the potentials have the same values as at the point."

The deduction which has had the widest application is that summarized in equation [233]. If we apply this to a component which is obeying the laws for an ideal gas we can relate density to pressure as follows

$$pv = nRT, \qquad *(1)$$

$$\gamma = \frac{nM}{v}, \qquad (2)$$

M being the molecular weight of the component, so that

$$\gamma = p\,\frac{M}{RT}. \qquad (3)$$

If p_0 be the pressure at some horizontal plane, the reference zero point from which we measure the height h, we can substitute in equation [233], integrate and obtain the famous

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* Since the temperature which appears explicitly in equations (1) to (10) of this article is in all cases the absolute temperature it seems best to conform to current usage by representing it by T.

hypsometric or *barometric* formula

$$p = p_0 e^{-\frac{Mg}{RT} h}, \tag{4}$$

which gives us pressure as a variable depending only on height.

The most famous application of this equation is in the study of variations in pressure of the earth's atmosphere with height. Galileo first pointed out that the atmosphere created pressure, and Périer proved that the pressure varied with height by means of his famous ascent of the Puy de Dôme, barometer in hand. Laplace[1] deduced the correct formula for the variation of pressure with height in his celebrated *Mécanique Céleste* and Gibbs showed that it took its place as part of the general thermodynamic scheme. As an example, substituting the numerical values $M = 29$ gm/mol, $g = 980$ cm/sec², $R = 8.31 \times 10^7$ erg/mol deg, $T = 300°$K, we find that at a height of 5000 meters the pressure has dropped to 56.5% of its value at the earth's surface.

It was also appreciated at rather an early date that the concentration of solute in a solution should vary with the height because of the influence of gravity. In the early part of the last century Beudant[2] claimed experimental evidence of this effect. Gay Lussac,[3] however, definitely proved that it was too small to be observed. He placed cylinders of various solutions in the cellar of the Paris observatory, and after a year's time analyzed the top and bottom portions, finding no differences in concentration. Many years later Gouy and Chaperon[4] showed by calculations that for solutes of ordinary molecular weight the effect is negligibly small.

Though ordinary solutions failed to show the effect, the advent of colloidal solutions opened up new possibilities in this direction. Einstein[5] pointed out that a colloidal suspension should obey the same kinetic laws as an ordinary solute, and a startling experimental confirmation was provided by Perrin.[6] He allowed a suspension of gamboge to come to equilibrium after settling for some time and then actually counted the number of particles of a given radius (i.e., similar molecular weight) occurring at different levels. In order to test his result it is convenient to modify equation (4) slightly. Since the osmotic pressure p will be related to the number of particles per cu. cm n by

$$p = \frac{RT}{N} n, \tag{5}$$

in which N is Avogadro's number, we may substitute n for p, and n_0 for p_0. We must also bear in mind that in this case the force of gravity enters because of the difference in density of the particles and the solvent. The depressant force will therefore be not Mg but $\frac{4}{3}\pi r^3 N(\rho_p - \rho_s)g$, where r is the radius of the particle and ρ_p and ρ_s the densities of the particle and solvent. Equation (4) then becomes

$$n = n_0\, e^{-\frac{N}{RT}\frac{4}{3}\pi r^3 (\rho_p - \rho_s)(h - h_0)g}. \tag{6}$$

TABLE I

Sedimentation Equilibrium in a Gamboge Suspension

x	n	
	Obs.	Calc.
x_0	100	. . .
$x_0 - 25\mu$	116	119
$x_0 - 50\mu$	146	142
$x_0 - 75\mu$	170	169
$x_0 - 100\mu$	200	201

Table I shows the variation in the number of particles over a microscopic range as determined by actual counting and as calculated from equation (6). Westgren[7] made similar measurements with gold sols and obtained even better agreement. His results are given in Table II.

It is evident from an examination of the derivation of equations [233] and (4) that the force involved does not necessarily have to be that of gravity. A system of particles acting under any uniform field of force will obey the same laws. For example, the distribution of particles under a centrifugal force provides a means of studying this sort of phenomenon.

Bredig[8] was the first to show that centrifugal force does produce changes in pressure. By centrifuging gases in a tube containing several chambers joined by capillary tubes, he showed that the pressure in the outermost chamber was greatest.

Lobry de Bruyn and van Calcar[9] produced the same sort of effect in solutions, showing that solute is driven away from the axis of rotation. They were able by centrifuging to crystallize out a third of the solute from a saturated solution of sodium sulfate. It was not possible however to get a quantitative confirmation of the thermodynamic equation.

TABLE II

SEDIMENTATION EQUILIBRIUM IN A GOLD SOL

Radius of Particles: $21m\mu$			Radius of Particles: $26m\mu$		
x	n		x	n	
	Obs.	Calc.		Obs.	Calc.
0μ	889	886	0μ	1431	1176
100	692	712	50	1053	909
200	572	572	100	779	702
300	426	460	150	532	555
400	357	369	200	408	419
500	253	297	250	324	324
600	217	239	300	254	250
700	185	192	350	189	193
800	152	154	400	148	149
900	125	124	450	112	115
1000	108	100	500	93	89
1100	78	80			

A series of brilliant experiments of this sort has recently been performed by The Svedberg and his associates in connection with the development of the ultra-centrifuge. While the major part of the work has been concerned with diffusion rather than equilibrium, certain aspects illustrate in a beautiful manner the relations which we have been considering.

In the first place it is very important to know the relative distribution of the particles in equilibrium even if the study is mainly concerned with diffusion which will not be continued long enough to bring about equilibrium. In calculating their distribution in the ultra-centrifuge where forces 5000 times that of gravity are encountered, one cannot consider the force as constant but must take into account the variation of force with distance from the axis of rotation. Using concentration c instead of pressure, the distance x from the axis of rotation instead of height, and the force due to the difference in density between particle and solvent instead of $g\gamma$, equation [233] becomes

$$dc = -\frac{N}{RT}\,\tfrac{4}{3}\,\pi r^3\,(\rho_p - \rho_s)\,\omega^2 c\,x dx, \tag{7}$$

where ω represents the angular velocity.

If we wish to get the concentration at different points in a tube such as might be placed in the ultra-centrifuge, we may let x_0 represent the end of the tube furthest from the axis, i.e., the bottom of the cell. Then on integrating we obtain

$$c_x = c_0 e^{-\frac{N}{RT}\frac{4}{3} r^3 (\rho_p - \rho_s)\omega^2 \left(\frac{x_0^2 - x^2}{2}\right)}. \tag{8}$$

Figure 1 shows the distribution for various particle sizes as calculated by Svedberg from this equation, letting $x_0 = 5.2$ cm. and $\omega = 190\pi$ per sec.

We may write equation (7) also in the form

$$\frac{dc}{c} = -\frac{M(1 - V\rho_s)}{RT}\,\omega^2\,x\,dx, \tag{9}$$

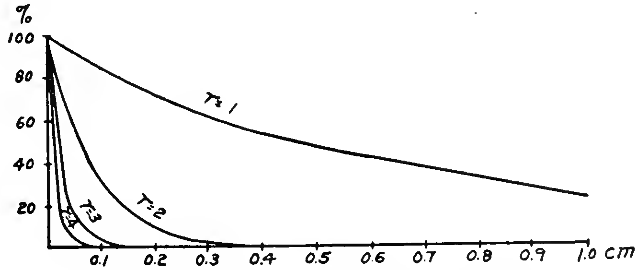
where V is the partial specific volume of the solute. Integrating and solving for M, we get

$$M = \frac{2\,RT\,ln\,(c_1/c_2)}{\omega^2(1 - V\rho_s)\,(x_1^2 - x_2^2)}. \tag{10}$$

In this way the measurements of concentration at equilibrium may serve as a means of calculating the molecular weight of the particles.

Svedberg and Fåhraeus[10] made observations of this sort on hemoglobin. The solution of hemoglobin was placed in the centrifuge tube and photographs were made after various intervals of time showing the density of the solute at various distances from the axis of rotation. By analyzing these photographs with a photo-densitometer very accurate measurements of concentration were secured. Table III shows how the molecular weight was calculated from the change in concentration with distance for one set of experiments.

During the course of the investigation the initial concentration was varied from 0.5 to 3.0 gm. of hemoglobin per 100 cc. of solution, the length of the column from 0.25 cm. to 0.8 cm. and the speed of revolution from 7200 to 10,000 r.p.m. without producing any marked change in the calculated molecular weight.*



r=radius of particles in millimicrons (10^{-7} cm).

FIG. 1

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* An important contribution to this subject has recently been made by Kai O. Pedersen, *Z. physik. Chem.* **170A**, 41 (1934). It consists of a study of the radial variation of the concentration of salts in aqueous solution at equilibrium in a centrifugal field of force of the order of 2×10^5 times the earth's gravitational field. The change in concentration is measured by photographing the distortion of the image of a scale observed through the column of liquid rotated at a speed of 55000 r.p.m. in the usual manner. From the displacement of the scale lines due to the change in the index of refraction, one can calculate the radial variation in concentration due to the force field. A thorough discussion is given of the thermodynamic relations involved, and an equation is derived relating the molecular weight to the concentration changes observed and the activity coefficients. The average error of the molecular weights so determined is about ten per cent. If it is possible to obtain accurate values of the absolute concentration changes this may be a valuable means of calculating activity coefficients.

In addition to these experiments, which have involved true equilibrium, mention should be made of the interesting determinations of the effect of gravity on the electromotive force of cells.

Tolman[11] has shown that much valuable information on the nature of solutions can be obtained by studying the electromotive force which is produced when a solution of uniform concentration is placed in a centrifugal force field. This e.m.f. is due, of course, to the fact that the concentration is *uniform*, and would disappear if diffusion were allowed to bring the concentration to the equilibrium values, such as we have been calculating from the above equations.

The same principles have also been applied to particles in electric and magnetic fields, notably in the work of Langevin[12] on the nature of paramagnetism.

TABLE III

THE MOLECULAR WEIGHT OF HEMOGLOBIN AS DETERMINED BY SEDIMENTATION EQUILIBRIUM

x_1	x_2	c_1	c_2	$M \times 10^{-3}$
cm.	*cm.*	*gm. per 100 cc.*	*gm. per 100 cc.*	
4.61	4.56	1.220	1.061	71.30
4.56	4.51	1.061	.930	67.67
4.51	4.46	.930	.832	58.33
4.46	4.41	.832	.732	67.22
4.41	4.36	.732	.639	72.95
4.36	4.31	.639	.564	60.99
4.31	4.26	.564	.496	76.57
4.26	4.21	.496	.437	69.42
4.21	4.16	.437	.388	66.40

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J

FUNDAMENTAL EQUATIONS OF IDEAL GASES AND GAS MIXTURES

[*Gibbs, I, pp. 150–184; 372–403*]

F. G. KEYES

I. General Considerations (*Gibbs, I, 150–164*)

1. Pure Ideal Gases. The response of gases to changes of pressure, temperature and volume was a subject of the greatest interest during the latter half of the 17th century and continuing through the 18th and 19th centuries. Boyle's work, appearing in 1660, and Mariotte's investigations (1676) established as a property of several gases the constancy of the pressure-volume product at constant temperature. Not until the beginning of the 19th century, however, was definite and sufficiently exact information secured regarding the volume-expansion law with temperature for constant pressure, and the pressure-increase law with temperature for constant volume. A knowledge of the latter laws, now known under the name of Gay-Lussac[1,2] as well as the Boyle-Mariotte law, was necessary to understand experiments on the relations of the volumes of chemically combining gases,—experiments the interpretation of which proved of such incisive importance to chemistry as a whole. It remained for Amedéo Avogadro[3] to draw the important inference from these investigations that the number of particles or molecules is the same for different gases of equal volume, the temperature and pressure being the same for all. There results then the remarkably simple expression for the physical behavior of pure gases

$$\frac{pv}{\theta} = \text{universal constant,} \tag{I}$$

where v is the volume of a "gram molecule" and Θ would have referred in the first half of the last century, to the absolute temperature as measured by a mercury thermometer. The upper limit of pressures was low and the precision of measurement, moreover, hardly sufficient to make evident the limits of validity of the relation (I) for describing the behavior of actual gases. The extraordinarily ingenious and precise measurements of Regnault were the first which showed the degree of inexactness which must be accepted. Thus for the gases air, nitrogen, carbon dioxide and hydrogen, compressed to a twentieth of the volume at zero degrees and one atmosphere, the following pressures were found:

	Air	N_2	CO_2	H_2
Pressure at $\frac{v_0}{20}$ atm.....	19.72	19.79	16.71	20.27
Percent deviation from Equation (I).........	−1.4	−1.1	−16.45	+1.4

At one-fifth of the volume, however, the magnitudes of the deviations reduce to −0.4, −0.3, −3.4 and +0.24 percent, respectively. Thus with respect to pressures at constant temperature Regnault's classical investigations, of which the foregoing is but a fragment, make it clear that equation (I) is to be regarded strictly as the expression of a limiting law to which actual gases may be expected to conform as the pressure is indefinitely reduced. The gas-thermometric investigations of Regnault[4] and subsequently others[5] showed that the volume-temperature coefficient at constant pressure, and similarly the pressure-temperature coefficient at constant volume, tend to an identical constant with diminishing pressure, thereby establishing the universality of the temperature scale definable by equation (I) for $p \rightarrow 0$. In addition, researches of Joule and later of Joule and Thomson proved that the internal energy of a gas at very low pressures is a temperature function only. The investigations of the heat capacities of gases had, moreover, shown in many cases, particularly for the gases whose critical temperatures were low, that the temperature coefficients were very small indeed.

The complete concept, therefore, of the perfect gas, accepted by Clausius and here taken by Gibbs, is defined by the first three equations of this section. For convenience of reference they will be designated as follows:

$$pv = at, \tag{II}$$
$$d\epsilon = c\,dt, \tag{III}$$
$$\epsilon = ct + E. \tag{IV}$$

It is noted that the heat capacity employed is that at constant volume rather than that at constant pressure. There is wisdom in the choice, for the former is the simpler quantity, and while it must usually be derived from measurements at constant pressure in default of direct measurements at constant volume, nevertheless this reduction may be carried out once for all as a special operation in preparing heat capacity data for use in the applications of thermodynamics where gases are involved. It is, moreover, not difficult to show that many applications of thermodynamics involving liquids and solids proceed very advantageously where the constant-volume heat capacity is employed.

2. Mixtures of Ideal Gases. The question of greatest importance in all detailed applications of thermodynamics is that of determining the laws to be employed in representing the physical behavior of mixtures of gases. Until the various aspects of this problem are resolved no real progress with applications of the general theory becomes possible, and it is for this reason that Gibbs took the greatest care to investigate all ramifications of this far from simple matter. It also seems evident from the statements and form of this section that Gibbs was seeking for a principle which would carry further than the popularly phrased statement of Dalton's law or rule for mixtures of gases. Indeed he found a statement of Dalton's law ("Gibbs-Dalton law") which he showed to be "consistent and possible" for mixtures of gases which are not ideal.*

3. Ideal Gas Concept as Related to the Behavior of Actual Gases under Diminishing Pressure. Because (II), (III), (IV) are believed to be limiting laws valid for infinitely extended volumes it is desirable to review briefly the circumstances surrounding the behavior of important functions along the path by which reduction of pressure to zero takes place. Consider in this connection, for example, the Joule-Thomson experiment. The effect is given by the thermodynamic equation,

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* A test of this law has recently been made. See reference (6).

$$\left(\frac{dt}{dp}\right)_\chi c_p = t\left(\frac{\partial v}{\partial t}\right)_p - v = -\left(\frac{\partial v\tau}{\partial \tau}\right)_p, \tag{V}$$

where c_p designates the constant-pressure heat capacity, χ the "heat content" ($\epsilon + pv$) and $\tau = t^{-1}$. The existing data show that the right hand member does not vanish as p goes to zero but on the contrary becomes constant and independent of the pressure. Joule and Thomson deduced, however, that the effect varied inversely as t^2 at low pressures, which requires the following relation between p, v, and t:

$$v = f(p)t - \frac{a'}{t^2} \tag{VI}$$

or

$$\frac{v}{f(p)t} = \left(1 + \frac{a'}{t^2 v}\right)^{-1}.$$

Clearly the condition that (II) be applicable at every temperature is that $f(p)$, as is possible, may be taken to be R/p for $v \to \infty$.

On the other hand, the change of energy with volume,

$$\left(\frac{\partial \epsilon}{\partial v}\right)_t = -\left(\frac{\partial p\tau}{\partial \tau}\right)_v,$$

has been shown in the case of one substance[7] to vary as the density squared (at low pressures), which may be regarded as a verification by experiment of equation (IV) since $(\partial\epsilon/\partial v)_t \to 0$ as the density diminishes. The consequence of this is that $\epsilon = f(t)$ and that $p = f(v)t$. Taking into account the validity of Boyle's law as an exact expression of physical behavior for $p \to 0$ the latter relation leads to equation (II). The quantity

$\left(v - \frac{Rt}{p}\right)$ is also well known[8,9] to proceed to a finite limit for $p \rightarrow 0$. The quantity is in fact never zero except at a unique temperature, characteristic of each pure substance (Boyle—point). It follows, therefore, that $(pv - Rt)$ vanishes at all temperatures when $p \rightarrow 0$.*

4. Constancy of Specific Heat. The justification for defining a perfect gas by means of equations (II), (III) and (IV) is complete except as regards the absolute constancy of specific heat. Experiment has proved to a high degree of precision that the constant-volume heat capacities of monatomic gases, at low pressures, are independent of temperature. Thus c for argon is very closely 2.98 from below zero degrees to about 2000°C. However, in the case of diatomic gases the temperature dependence, while small at ordinary temperatures, is significant and the modern quantum theory is eminently satisfactory in the account it provides of the course of c for hydrogen from a value of 2.98 at low temperatures to a value of 4.98 at room temperatures. Molecules of a higher order of complexity have a correspondingly large positive temperature coefficient above zero centigrade.

5. Concluding Statement. We may therefore sum up the present position with respect to the validity of the relations (II), (III) and (IV) by stating that (II) may be assumed to have been abundantly shown by experiment to correspond with reality as a limiting law for computing pressures for all pure gases. The independence of c with respect to temperature is, however, only true on the basis of present experience for monatomic gases, and the magnitude of the temperature coefficient of the heat capacity for all higher order molecules is large according to the order of complexity.

6. Comment on Gas Law for Real Gases. A discussion of the section might be carried forward from this point without explicit reference to an equation of state of greater complexity than (II). Gibbs has, however, adopted a definite hypothesis, the Gibbs-Dalton law (Gibbs, I, 155, beginning line 7), the implications of which can only be fully developed by using an equation connecting p, v, t and the mass, which is valid at sensible pressures (one atm. for example). Such an equation may be readily obtained by the use of equation [92] of Gibbs' *Statistical Mechanics*[10], viz.,

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* It should be understood that temperatures greater than absolute zero are referred to throughout in the considerations above.

$$p = \frac{at}{v - B}, \quad B = -2\pi n \int_0^{\infty} (e^{-\epsilon/kt} - 1)\, r^2 dr. \quad \text{(VII)}$$

Employing the van der Waals' model,[11] for example, there is obtained the following simple equation for B at low pressures

$$B = \beta - \frac{A}{at}\left(1 + \frac{\alpha_1 A}{at\beta} + \frac{\alpha_2 A^2}{a^2 t^2 \beta^2} \cdots\right). \quad \text{(VIIa)}$$

It is true that the van der Waals model is often inadequate (case of helium, neon) but it gives results sufficiently in accord with fact for the purposes of this section to make it unnecessary to deal with the considerably more involved expression following from a model more in accord with contemporary ideas of atomic and molecular structure [12, 13, 14, 15, 16, 17, 18]. The quantity B of (VIIa) is a pure temperature function in which β, A, α_1 and α_2 are constants.

Gases, it is apropos to state, may be sorted into two classes, those which have a permanent electric moment in the sense of the dielectric constant theory and those which have not. In the former class[19] are found water, ammonia, the hydrohalogen acids, sulphur dioxide, the alcohols, etc., while the noble gases, nitrogen, hydrogen, oxygen, methane have no moments. The simpler more symmetrical structure of the latter substances is reflected in their physical and quasi-chemical behavior (adsorption for example). Thus the departure from relation (II) for the latter gases is less, and it is not necessary to retain many terms of the bracketed part of (VIIa). Molecules having permanent moments exhibit on the contrary great departure from relation (II).*

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* At zero degrees and one atmosphere nitrogen has a pressure less than that calculable from (II) by about one twentieth of one percent. Am-

In many cases of interest in the application of Gibbs' theory to gaseous equilibria, the temperature of measureable reaction rate and practically significant concentrations of the products of the reaction are sufficiently high to enable an equation of essentially the type of (VII), (VIIa), to be used without involving too serious error[20, 21, 22, 23]. Every purpose will be served in what follows by omitting all terms in the brackets in (VIIa) following the one having the coefficient α_1.

7. Choice of Units of Mass and Energy. The equations (II) to (IV) of Gibbs refer to "a unit" of gas and the gram or gram mol might equally well be employed. We will consider one gram as the unit quantity in what immediately follows and the gram mol in those instances where convenience is thereby better served. The unit of energy will be the mean gram-calorie equal to 4.186 abs. joules where practical applications require specification of the unit. The temperature scale will be that of the centigrade scale given by the platinum resistance thermometer plus 273.16, and the pressure unit the international atmosphere, volumes being taken in cubic centimeters per gram or gram mol.

8. Definition of Temperature. It is noted that the temperature is defined by the perfect gas (Gibbs, I, 12–15) or quite simply, if the heat capacity c is assumed an invariable constant, by the energy equation. Taking equation [11] (Gibbs, I, 63) for the energy, $d\epsilon = t d\eta - p dv$, temperature and pressure may be expressed in terms of the energy ϵ, the volume, and the appropriate constants. From (IV) and (II) there result

$$t = \frac{\epsilon - E}{c}, \qquad (1)\ [257]$$

$$p = \frac{a}{v}\,\frac{\epsilon - E}{c}, \qquad (2)\ [258]$$

---

monia under the same conditions of temperature and pressure has a pressure less than that given by (II) by one and one-half percent, and in conformity with the modern theory of cohesive and repulsive forces the bracketed expression on the basis of a van der Waals model becomes more complicated. However, in the case of dipole gases at ever higher temperatures (VII) tends to a simpler form on account of the diminishing relative importance of those terms arising from the presence of the permanent dipole.

and substitution in [11] leads to a relation in which the variables separate. Integration then results in equation [255]. Evidently since c, except for the monatomic gases, is in general a quite complex function of the temperature it is not practical to write t as a function of the energy in a fundamental equation* in the variables energy, entropy and volume.† If c is taken as a function of temperature, $f(t)$, the equation for the entropy may be readily obtained from [11] for

$$d\eta = \frac{d\epsilon + pdv}{t} = \frac{f(t)dt + pdv}{t},$$

or

$$\eta = \int f(t)\,\frac{dt}{t} + a \log v + H. \tag{3}$$

The forms of $f(t)$ which are known, as for hydrogen, make it practically impossible to eliminate t to give an equation in the variables ϵ, η and v.

9. Constants of Energy and Entropy. The remarks following equation [255] are important, for the assigning of the constants of entropy, H, and of energy, E, is a matter of importance in all cases of chemically interacting components. The conventions which have been used are, however, somewhat varied; thus Lewis and Randall[24] define a standard state in terms of unit fugacity of the elements; and 0° on the absolute or Kelvin scale and one atmosphere[25] has also been proposed. There is much advantage[23] in adopting the actual state of the gas at 0° and one atmosphere, but any of the proposed systems is a possible one so long as interest centers on the treatment of ordinary chemical reactions by the two empirical principles of thermodynamics.‡

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* See footnote, Gibbs, I, 88.

† Gibbs has discussed the advantages of volume and entropy as independent variables (Gibbs, I, 20).

‡ The statistical mechanics analogue of the entropy may for example be easily computed from equation [92] of Gibbs' Statistical Mechanics (Gibbs, II, Part I, 33) for the simple case of a gas assumed to be composed of structureless mass points. Before making the computation, note should be taken of the fact that equation [92] may be dimensionally satisfied by dividing the right hand member under the logarithm by Planck's constant h raised to the $3n$th power.

10. ψ Function for an Ideal Gas. On substituting its equivalent t for $\dfrac{\epsilon - Em}{cm}$ in [255], and solving for η there results,

$$\eta = mc \log t - ma \log \frac{m}{v} + mH, \qquad (4)\ [255]$$

$$\psi = -\Theta \log \left(\frac{m}{h}\right)^{3n} \int \ldots \int e^{-\epsilon/\Theta} d\dot{x}_1\, d\dot{y}_1\, d\dot{z}_1,\, dx_1\, dy_1\, dz_1. \qquad \text{(a)}$$

If ϵ is given by $\dfrac{m}{2}\,(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ there results

$$\psi = -\Theta \log \left(\frac{2\pi m\Theta}{h^2}\right)^{\frac{3n}{2}} \cdot v^n. \qquad \text{(b)}$$

Applying the operation $-\dfrac{\partial}{\partial t}$ at constant volume and assuming $n\Theta$ given by at the following analogue of the entropy results:

$$\eta' = \tfrac{3}{2}\, a \log t + a \log v + \tfrac{3}{2}\, a \log \frac{2\pi mke}{h^2}. \qquad \text{(c)}$$

Here a definite value of the constant of entropy appears which bears a direct relation to the Nernst Heat Theorem and the so-called chemical constant[26, 27, 28]. Differentiation of equation (b) with respect to the volume at constant temperature and changing the sign gives the following expression for the pressure:

$$-\left(\frac{\partial \psi}{\partial v}\right) = p = \frac{n\Theta}{v} = \frac{a't}{v}. \qquad \text{(d)}$$

which is equation (II). Again, forming the energy by the operation

$$\left(\frac{\partial \psi \tau}{\partial \tau}\right)_v = \epsilon$$

where τ represents $k\Theta^{-1} = t^{-1}$, k being the Boltzmann constant (1.37×10^{-16} ergs/deg.) we obtain

$$\left(\frac{\partial \psi \tau}{\partial \tau}\right)_v = \epsilon' = \tfrac{3}{2}\, nkt = \tfrac{3}{2}\, c't. \qquad \text{(e)}$$

Here no constant of energy is assigned nor should a constant appear in view of the properties of a system of structureless mass points treated by classical statistical mechanics.

as the expression for the entropy of a mass m of the pure gas. Using this entropy equation and (IV) and substituting in [87] there is obtained

$$\psi = mct + mE - mct \log t - mat \log \frac{v}{m} - mHt, \qquad (5)\ [260]$$

which is identical except for slight rearrangements with [260]. Differentiation with respect to t at constant volume and applying a change of sign gives

$$-\left(\frac{\partial \psi}{\partial t}\right)_{v,m} = mc \log t + ma \log \frac{v}{m} + mH = \eta, \qquad (6)\ [262]$$

which is the entropy of the pure gas. The pressure is given likewise by changing the sign and differentiating with respect to volume at constant temperature, i.e.,

$$-\left(\frac{\partial \psi}{\partial v}\right)_{t,\,m} = \frac{mat}{v} = p. \qquad (7)\ [263]$$

The energy and heat capacity are formed by operating on $\psi t^{-1} = \psi \tau$, where τ represents reciprocal temperature, as follows:

$$\epsilon = \left(\frac{\partial \psi \tau}{\partial \tau}\right)_{v,\,m} = mct + mE, \qquad (8)$$

$$-\frac{\tau^2}{m}\left(\frac{\partial^2 \psi \tau}{\partial \tau^2}\right)_{v,\,m} = c. \qquad (9)$$

Finally the chemical potential may be found by differentiation with respect to m, keeping v and t constant,

$$\left(\frac{\partial \psi}{\partial m}\right)_{v,\,t} = \mu = ct - ct \log t - at \log \frac{v}{m}$$
$$+ at - Ht + E. \qquad (10)\ [264]$$

Thus every quantity of thermodynamic interest may be obtained from the Helmholtz free energy function ($\psi = \epsilon - t\eta$)

by simple differentiation. Gibbs has obtained the same result by comparing the terms of the total differential of ψ,

$$d\psi = \left(\frac{\partial\psi}{\partial t}\right)_{v,m} dt + \left(\frac{\partial\psi}{\partial v}\right)_{t,m} dv + \left(\frac{\partial\psi}{\partial m}\right)_{v,t} dm,$$

and

$$d\psi = -\eta dt - pdv + \mu dm, \qquad (11)\ [88]$$

with equation [261].

11. ζ Function for an Ideal Gas. Turning to the zeta function* [91], $\zeta = \epsilon + pv - t\eta$, we may form the function in terms of pressure, temperature and the mass of a pure perfect gas with the following result:

$$\zeta = mct + mE + mat - mct \log t - mat \log \frac{at}{p} - mHt. \qquad (12)\ [265]$$

By differentiation the following equations are obtained:

$$-\left(\frac{\partial\zeta}{\partial t}\right)_{p,m} = \eta = mc \log t + ma \log\frac{at}{p} + mH, \qquad (13)\ [266]$$

$$\left(\frac{\partial\zeta}{\partial p}\right)_{t,m} = v = \frac{mat}{p}, \qquad (14)\ [267]$$

$$\left(\frac{\partial\zeta\tau}{\partial\tau}\right)_{p,m} = mct + mE + mat = m\epsilon + mat, \qquad (\text{IVb})$$

$$\frac{1}{m}\left(\frac{\partial^2\zeta\tau}{\partial t\partial\tau}\right)_{p,m} = (c + a),$$

$$\left(\frac{\partial\zeta}{\partial m}\right)_{p,t} = \mu = ct - ct \log t - at \log \frac{at}{p} + at - Ht + E. \qquad (15)\ [268]$$

---

* This function is called the "Free Energy" by Lewis and Randall in their treatise *Thermodynamics and the Free Energy of Chemical Substances.*

The latter equation for μ is, as it should be,* identical with (10) [264], since at/p is equal to v/m.

By setting $\left(\frac{H-c}{a} - 1\right)$ and $\left(\frac{c}{a}\right) + 1$ equal to the constants κ_1 and κ_2, (15) [268] may be written

$$p = a \cdot e^{\kappa_1} t^{\kappa_2} e^{\frac{\mu - E}{at}}, \tag{16) [270}$$

or the density ρ is given by

$$\rho = e^{\kappa_1} t^{\kappa_2 - 1} e^{\frac{\mu - E}{at}}. \tag{17) [270}$$

12. χ Function for an Ideal Gas. The equation for χ† is likewise readily formed from equations (II) and (IV). Thus

$$\chi = \epsilon + pv = m(c + a)t + mE, \tag{18) [89}$$

and on differentiating this equation there results, using [86],

$$d\chi = td\eta + vdp + \Sigma\, \mu dm, \tag{19) [90}$$

showing that the independent variables are the entropy, pressure and mass. From (18) [89] there is obtained $t = \frac{\chi - mE}{m(c + a)}$, and using the total differential of [89], with $td\eta$ replacing $d\epsilon + pdv$, we have

$$d\chi = \frac{\chi - mE}{m(c + a)} \cdot d\eta + \frac{\chi - mE}{(c + a)} \cdot \frac{adp}{p}$$

or

$$m(c + a)\frac{d\chi}{\chi - mE} = d\eta + am\frac{dp}{p}, \tag{20}$$

which on integration, and using the entropy constant H, gives [271], or

---

* See equations [104], Gibbs, I, 89.

† This quantity is frequently referred to as the "total heat," a somewhat misleading term. It is also often designated by the symbol, H.

$$\chi = mE + m(c + a)\, e^{\frac{\eta - mH}{m(c+a)}} \left(\frac{p}{a}\right)^{\frac{a}{c+a}}, \tag{21}$$

$$\left(\frac{\partial \chi}{\partial p}\right)_{\eta,\, m} = e^{\frac{\eta - mH}{m(c+a)}} \cdot \left(\frac{p}{a}\right)^{\frac{a}{c+a}} \cdot \frac{ma}{p}, \tag{22}$$

but

$$e^{\frac{\eta - mH}{m(c+a)}} \left(\frac{p}{a}\right)^{\frac{a}{c+a}} = \frac{\chi - mE}{m(c + a)} = t, \tag{23}$$

which gives

$$\left(\frac{\partial \chi}{\partial p}\right)_{\eta,\, m} = \frac{mat}{p} = v. \tag{24}$$

It is also easily shown that $\left(\frac{\partial \chi}{\partial \eta}\right)_{p,\, m} = t$, while $\left(\frac{\partial \chi}{\partial m}\right)_{\eta,\, p}$ gives an equation for μ identical with [268].

13. Vapor Pressures of Liquids and Solids. The footnote (Gibbs, I, 152) concerning the general problem of vapor pressures is important, for not only is a relation between pressure and temperature often required for pure liquids or solutions in equilibrium with a vapor phase, but equally important is the large class of compounds of solids with volatile components, as for example the salt hydrates, salt compounds with ammonia, sulphur dioxide, and numerous similar compounds. Innumerable formulae for the vapor pressure of liquids have been suggested since the middle of the last century. Those that do not have a purely empirical origin may be obtained from the Clapeyron equation

$$\lambda = t\,\frac{dp}{dt}\,(v_1 - v_2),$$

using various assumptions. Thus if the specific volume of the liquid v_2 is neglected, the vapor, v_1 assumed a perfect gas, and the heat of evaporation, λ supposed a linear function of the temperature, there results

$$\lambda_0 + \alpha t = t\,\frac{dp}{dt} \cdot \frac{at}{p}, \tag{25}$$

where λ, the heat of evaporation, is expressed in terms of a constant λ_0 and α. One obtains on solving (25)

$$\log p = -\frac{\lambda_0}{at} + \frac{\alpha}{a}\log t + \text{constant}, \tag{26}$$

which is of the same form as Gibbs' equation [269]. The procedure adopted in the footnote, however, brings to the fore the precise nature of the assumptions upon which the resulting vapor pressure formula rests. Moreover, it is more direct than the above treatment, as may be easily shown.

For the single accent phase (vapor) and the double accent phase (condensed substance) we have*

$$\left.\begin{aligned} -v'\,dp + \eta'\,dt + m'\,d\mu' &= 0,\\ -v''dp + \eta''dt + m''d\mu'' &= 0. \end{aligned}\right\} \tag{27}$$

Gibbs proceeds to solve these equations and, from the equilibrium condition $d\mu' = d\mu''$, to extract the pressure as a function of t. But on solving the above pair of equations subject to the same equilibrium condition there results

$$\begin{vmatrix} v' & m' \\ v'' & m'' \end{vmatrix} dp = \begin{vmatrix} \eta' & m' \\ \eta'' & m'' \end{vmatrix} dt. \tag{28}$$

Expanding the determinants gives

$$(v'm'' - v''\,m')\frac{dp}{dt} = (\eta'm'' - \eta''m'). \tag{29}$$

If $m' = 1 = m''$, and $\eta' - \eta''$ is set equal to $\frac{\lambda}{t}$, the entropy of transfer from the first to the second phase, we have the Clapeyron equation

$$(v' - v'')\frac{dp}{dt}t = \lambda,$$

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* See equation [124], Gibbs, I, 97.

from which the vapor pressure equation was obtained above. Gibbs preferred to proceed directly with the μ equations in establishing his vapor pressure relation.

It will be noted that Gibbs has assumed that the heat capacity k of the liquid is independent of the temperature. In addition it is assumed that the internal energy is a constant. It is in this way that the simple expression for the entropy $\eta = \log t + H'$ is obtained. These assumptions are, however, far from being true if a range of temperature is considered, as a glance at the data for the heat capacities of liquids shows. As compared with the vapor at moderate pressures most of the internal energy of a liquid is molecular potential energy and $t\left(\frac{\partial p}{\partial t}\right)_v - p$ is very large. Ether, for example, at -50 has a specific volume of 1.265 c.c. per gm., and $t\left(\frac{\partial p}{\partial t}\right)_v - p$, equivalent to $\left(\frac{\partial \epsilon}{\partial v}\right)_t$, amounts to 2780 atmospheres. The same quantity for the vapor in equilibrium with the liquid at -50 is not far from 1.5×10^{-5} atm. For short ranges of temperature along the saturation curve the Gibbs' assumption is in many cases admissible where only modest accuracy is required. The subject of vapor pressure representations on the lines of Gibbs' treatment has recently been fully developed by L. J. Gillespie.[29]

It is worth pointing out that Gibbs' treatment indicates the rôle played by the entropy constants in the constant of the vapor pressure relation. The heat theorem of Nernst is also closely related to the constants of the vapor pressure-temperature equation. To obtain, however, constants which are really characteristic of pure substances requires very reliable data at low pressures and skillful treatment of the data in formulating an equation [30, 31, 32, 33, 34, 35].

The treatment of the case where a gas is dissolved in a liquid is also touched upon by Gibbs in the latter part of the footnote. It is assumed that the vapor pressure of the liquid absorbing the gas is small enough to be neglected. However, while the latter approximation may be satisfactory, as for example with carbon dioxide at one atmosphere dissolving in water at zero degrees (vapor pressure of water 0.006 atm.), in many cases the solubility may be large enough to affect the vapor pressure considerably. The solubility of carbon dioxide in fact is sufficient to change the thermodynamic potential of the water considerably as the pressure of the carbon dioxide rises. There are several other factors to be considered if the case is to be treated with some degree of completeness, but for this a more extensive knowledge would be required than is at present available of the potentials of the components in the liquid mixture, and of the gas phase.

Nothing is very definitely known about the energy of mixtures of liquids or the entropy of a liquid mixture as a function of the entropies of the components. It may be assumed, however, that ζ for a mixture of liquids is of the same general form as that for the separate components. Moreover, if one or several components are present in small quantity the coefficients of the ζ equation of the mixture may be confidently assumed to be linear in the masses of the soluble constituents, on the ground that any continuous and differentiable function of a variable is linear in the limit of small values. It is in this sense that the second equation on p. 154 of the footnote should be understood in its practical applications. The remaining steps lead easily to the equation for the pressure of the dissolved gas as a function of the temperature. The values of the constants A, B, C and D will be constant for an invariable composition of the liquid solution. Differentiating the log (p/a) equation with respect to temperature at constant composition, and neglecting the term Dp/t which is small at low pressures, there is obtained

$$t^2\left(\frac{\partial \log p}{\partial t}\right)_c = C - Bt. \tag{30}$$

This quantity is proportional to the energy required to transfer unit mass of the dissolved gas to the gas phase under equilibrium conditions.

It is clear from the discussion above that a basis is here indicated for a theory of dilute solutions, for the treatment is by no means restricted to the case of gaseous substances which dissolve. Moreover, it will be observed that the latter case is capable of a considerably more detailed treatment along the lines laid down by Gibbs. Thus it would be easy to include in the discussion the effect of the dissolved gas, and the gas in the gas phase, on the vapor concentration of the vapor emitted by the solvent. For this purpose use would be made of the italicized statement (Gibbs, I, top of page 155) together with an equation for the gas and vapor, such, for example, as (VIIa).

14. Effect of the Presence of a Neutral Gas on Vapor Pressure. The paragraph beginning on p. 154 discusses the old observation that, for example, the vapor pressure of a mixture of water and benzene is about the sum of the vapor pressures of each pure liquid at the temperature of the mixture. Since, however, the pressure on the liquid phase is greater than if either were alone present the liquids must be compressed. The nature of the effect of a pressure applied to the liquid phase and its magnitude may be obtained by applying the equation [272] obtained from equation [92] (Gibbs, I, 87). Taking the temperature constant and assuming equilibrium conditions there results

$$d\zeta = (v dp + \mu_1 dm_1)_t. \tag{31}$$

But

$$\partial\zeta = \left(\frac{\partial\zeta}{\partial p}\right)_{t,\,m} dp + \left(\frac{\partial\zeta}{\partial m_1}\right)_{p,\,t,\,m} dm_1, \tag{32}$$

and, since p and m_1 are independent variables,

$$\left(\frac{\partial}{\partial m_1}\left(\frac{\partial\zeta}{\partial p}\right)_{t,\,m}\right)_{p,\,m} = \left(\frac{\partial}{\partial p}\left(\frac{\partial\zeta}{\partial m_1}\right)_{p,\,t,\,m}\right)_{t,\,m}. \tag{33}$$

Comparing equations (31) and (32) the latter may be written

$$\left(\frac{\partial v}{\partial m_1}\right)_{p,\,t,\,m} = \left(\frac{\partial\mu_1}{\partial p}\right)_{t,\,m}. \qquad (34)\ [272]$$

Similarly it may be shown from [88] that

$$\left(\frac{\partial\mu_1}{\partial v}\right)_{t,\,m} = -\left(\frac{\partial p}{\partial m_1}\right)_{t,\,v,\,m}. \tag{35}$$

The case of a pure liquid under pressure in excess of its vapor pressure at constant temperature can be treated quite simply using equation [272], provided it is assumed that the neutral ideal gas exerting the pressure on the liquid phase dissolves to a negligible extent, and that it is at the same time completely indifferent with respect to the vapor of the liquid. The latter restriction means, of course, not only that there must be no chemical action but also that the neutral gas must exert no "solvent" action with respect to the vapor.

For the vapor phase

$$\left(\frac{\partial \mu'}{\partial p}\right)_{t,\, m} = \left(\frac{\partial v'}{\partial m}\right)_{p,\, t}, \qquad (36)\ [272]$$

$$\left[\mu' = \int \left(\frac{\partial v'}{\partial m}\right)_{p,\, t} dp\right]_t, \qquad (37)$$

and for the liquid phase

$$\left(\frac{\partial \mu''}{\partial p}\right)_{t,\, m} = \left(\frac{\partial v''}{\partial m}\right)_{p,\, t}, \qquad (38)\ [272]$$

$$\left[\mu'' = \int \left(\frac{\partial v''}{\partial m}\right)_{p,\, t} dp\right]_t. \qquad (39)$$

But if equilibrium subsists, $\mu' = \mu''$, and moreover for a single pure phase, neglecting any possible complication due to the dissolved neutral gas,

$$\left(\frac{\partial v''}{\partial m}\right)_{p,\, t} = \frac{\partial}{\partial m}\left[(v''_{sat.} + \alpha p)m\right] = v''_{sat.} + \alpha p, \qquad (40)$$

where α is the compressibility of the liquid. Substituting $\frac{a't}{p}$ for $\left(\frac{\partial v'}{\partial m}\right)_{p,t}$ and integrating from the normal saturation pressure to the vapor pressure arising as a consequence of the changed potential of the compressed liquid in the case of the vapor, and from the normal saturation pressure to the pressure p of the neutral gas in the case of the right hand member, there is obtained

$$\log \frac{p}{p_{sat.}} = \frac{v''_{sat.}}{a't}(P - p_{sat.}) + \frac{v''_{sat.}\,\alpha}{2a't}(P^2 - p^2_{sat.})\,. \qquad (41)$$

Clearly $p > p_{sat.}$ for $P > p_{sat.}$ In the case of water at zero degrees under a pressure of 100 atm. there is obtained from (41)

$$p/p_{sat.} = 1.084.$$

The effect (Poynting effect) is small, but in exact determinations of vapor pressure, as by the "streaming" method, the effect must be considered (the vapor pressure of water at zero degrees is altered by roughly one tenth percent per atmosphere pressure).*

15. Defect in the Sum Rule for Vapor Pressures. The rule that the total pressure over a liquid phase mixture of mutually immiscible substances is given by summing the separate vapor pressures suffers from the fact that the gases are actually not ideal. Thus ammonia deviates at one atmosphere and zero degrees by 1.6 per cent from the ideal pressure. A mixture of nitrogen and ammonia in equal molal proportions, however, exerts a pressure, at zero degrees and about one atmosphere, not far from that calculated by the ideal gas law for mixtures. At higher or lower temperatures, nevertheless, the differences may be greater or less than that given by the latter law. As a general and approximate statement present knowledge warrants the conclusion that as far as low pressures are concerned, the order of accord of the actual behavior of pure gases and mixtures with the prediction of the perfect gas laws does not often exceed two percent from zero degrees to higher temperatures. Below zero the actual behavior of gases may show larger departure from the idealized state in special cases.

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* The method of passing a neutral gas over liquids and subsequently absorbing the vapor out of a known volume of the gas mixture has been much employed in determinations of vapor pressures where the latter are small. In utilizing such data to compute vapor pressures the relation of the mass of the vapor to the mass of the neutral gas must be accurately known. Frequently the perfect gas laws have been invoked to compute the pressure of the vapor in the neutral-gas-vapor mixture. If, however, precise results are desired this procedure is inexact owing to the fact that Dalton's rule of mixtures may not be as close an approximation as desirable. See Eli Lurie and L. J. Gillespie, *J. Am. Chem. Soc.*, **49**, 1146, (1927), also *Phys. Rev.*, **34**, 1605, (1929) and *Phys. Rev.*, **36**, 121, (1930). The disability of the method, due to the failure of Dalton's law, might be avoided by passing the neutral gas through a saturation apparatus containing pure water and then through a similar apparatus in series with the first but containing the solution of interest. The temperature of the latter could then be raised until suitable tests showed that the content of water in the neutral gas was the same after each saturation apparatus. Determinations at several temperatures would then establish the vapor pressures of the solution from the known values for pure water. It can be shown that strictly the "Dalton defect" is not precisely the same in both saturations because of the temperature difference, but the error thus made can be shown to be exceedingly small.

16. Gibbs' Generalized Dalton's Law. The rule of pressures stated in italics (Gibbs, I, 155, 7th line) is one of very great inclusiveness.* It leads, for example, to a proposition relative to the entropy of a gas in a mixture which is of very far reaching theoretical significance and practical importance. It contains and is also far more inclusive than Dalton's rule of partial pressures as commonly stated, since its consequences involve the proposition that the energy and all the thermodynamic functions of gases in a mixture are of the same value as though each gas alone occupied the same volume as the mixture, the temperature remaining unchanged. In the formulation there is incorporated also the idea of equilibrium, which does not appear to be associated with the usual statement of Dalton's Law. The significance of the equilibrium idea, both thermal and mechanical, must be emphasized because of its extensive importance in every application to which thermodynamics lends itself.

The Gibbs rule may be written, where the constants $\frac{H_1 - c_1 - a_1}{a_1}$ and $\frac{c_1 + a_1}{a_1}$ are represented by h_1 and C_1.

$$p = \sum\left(a_1 e^{h_1} t^{C_1} e^{\frac{\mu_1 - E_1}{a_1 t}}\right), \qquad (42)\ [273]$$

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* Gillespie (*Phys. Rev.*, **36**, 121, (1930)) has recently discussed in considerable detail the implications contained in Gibbs' italicized statement. It is shown that Gibbs' statement is, as would be expected, an approximation. It is, however, a useful rule, and is analogous to the Lewis and Randall rule of fugacities (Lewis and Randall, *Thermodynamics*, p. 226, 1923). The Gibbs rule and the fugacity rule often show deviations of opposite sign from the true pressures of binary mixtures.

but $(\mu_1 - E_1)/a_1 t$ may be formed from [268] and expressed as

$$e^{(\mu_1 - E_1)/a_1 t} = \frac{p_1}{a_1 e^{h_1} t^{C_1}}, \tag{43}$$

whence

$$(p = \Sigma p_1)_t,$$

or

$$p = \sum \frac{a_1 m_1 t}{v}. \qquad (44)\ [277]$$

The former may apply even when the gases are not ideal.

17. Entropy of an Ideal Gas Mixture. Differentiating (42), [273] and rearranging gives the following equations:

$$dp = \sum \left[\frac{a_1 e^{h_1} t^{C_1} e^{\frac{\mu_1 - E_1}{a_1 t}}}{t} \left(C_1 - \frac{\mu_1 - E_1}{a_1 t} \right) \right] dt + \sum \left[\frac{a_1 e^{h_1} t^{C_1} e^{\frac{\mu_1 - E_1}{a_1 t}}}{a_1 t} \right] d\mu_1, \tag{45}$$

$$dp = \sum \left[\frac{p_1}{t} \left(C_1 - \frac{\mu_1 - E_1}{a_1 t} \right) \right] dt + \sum \left[\frac{p_1}{a_1 t} \right] d\mu_1, \tag{46}$$

but by [98]

$$dp = \frac{\eta}{v}\, dt + \sum \frac{m_1}{v}\, d\mu_1, \tag{47}$$

whence using the value of

$$\frac{\mu_1 - E_1}{a_1 t} = -h_1 + \log \left(t^{-C_1} \frac{p_1}{a_1} \right)$$

from [269] there results

$$\frac{\eta}{v} = \sum \left[\frac{p_1}{a_1 t} \left\{ H_1 + (c_1 + a) \log t - a_1 \log \frac{p_1}{a_1} \right\} \right], \qquad (48)\ [274]$$

$$\left.\begin{aligned} \frac{m_1}{v} &= \frac{p_1}{a_1 t}, \\ \frac{m_2}{v} &= \frac{p_2}{a_2 t}, \text{ etc.} \end{aligned}\right\} \qquad (49)\ [275]$$

and

$$\eta = \sum \left(m_1 H_1 + m_1(c_1 + a_1) \log t + m_1 a_1 \log \frac{a_1}{p_1} \right).$$

Where v is the volume of the mixture the entropy becomes

$$\eta = \sum \left(m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{v}{m_1} \right). \qquad (50)\ [278]$$

The latter equation requires that the entropy of a gas in a mixture of volume v and temperature t be the same as though it existed alone at the volume v, the temperature remaining unchanged. The result may be exhibited in another form. The total volume v is given by the expression $\frac{t}{p}\,\Sigma a_1 m_1$ where p is the total pressure of the mixture. Substituting in (50) [278] there is obtained

$$\eta = \sum \left(m_1 H_1 + m_1\, c_1 \log t + m_1\, a_1 \log \frac{a_1 t}{p \dfrac{a_1 m_1}{\Sigma a_1 m_1}} \right), \qquad (51)\ [278]$$

but $p \dfrac{a_1 m_1}{\Sigma a_1 m_1}$ is a quantity which is called the partial pressure for the gas with subscript (1), i.e., p_1, and $\Sigma p_1 = p$, which is equation [273]. It follows then that if a gas exists in the pure state at pressure p and temperature t its entropy in the gas mixture of pressure p will differ from that in the pure state by $- m_1 a_1 \log \dfrac{a_1 m_1}{\Sigma a_1 m_1}$, which is the same thing as $- r_1/C \log x_1$, where $x_1 = \dfrac{r_1}{\Sigma r_1}$, the mol fraction, and $C^{-1} = M_1 a_1$ (see equation [298], Gibbs, I, 168), where M_1 is the molecular weight.

18. Implications of Gibbs' Generalized Dalton's Law Apart from Ideal Gas Behavior. The discussion, Gibbs I, 156–157, beginning eleven lines from the bottom of 156 and ending at the corresponding point on 157 comprises material and inferences following quite directly and simply from equations [273] to [278]. The last sentence is significant. "It is in this sense, (equations [282], [283]) that we should understand the law of Dalton, that every gas is as a vacuum to every other gas."

The statement that Gibbs' relations [282] and [283] are "consistent and possible" for other than ideal gases refers evidently to the belief that the relations in question, taken quite generally and without reference to the idealized gas laws, might lead to better accord with fact than would be possible with the latter. Thus the pressure of the individual gases composing the sum in the first of equations [282] may be any function of volume and temperature. By the use of (VII) for example, the total pressure would be written,

$$p = \sum \frac{a_1 t m_1}{v - B_1 m_1}. \tag{52}$$

The energy, entropy and ψ function then become

$$\epsilon = \sum \epsilon_1 = \sum m_1 \int_{t_0}^{t} c_1{}^* \, dt - \sum \frac{a_1 m_1{}^2 t^2}{v - B_1 m_1} \left(\frac{\partial B_1}{\partial t} \right) + \sum m_1 E_1, \tag{53}$$

$$\eta = \sum \eta_1 = \sum m_1 \int_{t_0}^{t} c_1{}^* \frac{dt}{t} + \sum m_1 a_1 \log \frac{v - B_1 m_1}{m_1} - \sum \frac{a_1 m_1{}^2 t}{v - B_1 m_1} \left(\frac{\partial B_1}{\partial t} \right) + \sum m_1 H_1, \tag{54}$$

$$\psi = \sum m_1 \int_{t_0}^{t} c_1{}^* dt + \sum m_1 E_1 - t \sum m_1 \int_{t_0}^{t} c_1{}^* \, dt/t - t \sum m_1 a_1 \log \frac{v - B_1 m_1}{m_1} - t \sum m_1 H_1. \tag{55}$$

Equation (53) may be established by starting with either of the equations

$$\left(\frac{\partial \epsilon}{\partial v} \right)_t = t \left(\frac{\partial p}{\partial t} \right)_v - p, \tag{56}$$

$$c = \left(\frac{\partial \epsilon}{\partial t}\right)_v = c^* + t\int_{\infty}^{v}\left(\frac{\partial^2 p}{\partial t^2}\right)_v dv. \tag{57}$$

Taking the first we find, using (VII),

$$\epsilon_1 = m_1 f(t) + \int_{\infty}^{v}\frac{a_1 m_1{}^2 t^2}{(v - B_1 m_1)^2}\left(\frac{\partial B_1}{\partial t}\right) dv + m_1 E_1, \tag{58}$$

where $f(t)$ is a pure temperature function. The integral may be taken from $v = \infty$ to v, resulting[36], if B is a pure temperature function, in

$$\epsilon_1 = m_1 \int_{t_0}^{t} c_1{}^* \, dt - \frac{a_1 m_1{}^2 t^2}{v - B_1 m_1}\left(\frac{\partial B_1}{\partial t}\right) + m_1 E_1, \tag{59}$$

where E_1 is a constant of reference for energy, and $c_1{}^*$ is the heat capacity for constant volume at infinitely low pressures,—a pure temperature function.

The other equation of the pair gives for ϵ

$$\epsilon_1 = m_1 \int_{t_0}^{t} c_1{}^* dt + \int_{t_0}^{t}\left[\int_{\infty} t\left(\frac{\partial^2 p}{\partial t^2}\right)_v dv\right] dt + m_1 E_1, \tag{60}$$

since

$$c = f(t) + t\int_{\infty}\left(\frac{\partial^2 p}{\partial t^2}\right)_v dv, \quad f(t) = c^*,$$

where c^* is the heat capacity of a gas at infinitely low pressure and is known to be a pure temperature function. But

$$t\left(\frac{\partial^2 p}{\partial t^2}\right)_v = \frac{\partial}{\partial t}\left[t\left(\frac{\partial p}{\partial t}\right)_v - p\right],$$

whence the second integral above becomes

$$\int_{t_0}^{t}\left[\int_{\infty}^{v} t\left(\frac{\partial^2 p}{\partial t^2}\right)_v dv\right] dt = \int_{t_0}^{t}\left[\int_{\infty}^{v}\frac{\partial}{\partial t}\left[t\left(\frac{\partial p}{\partial t}\right)_v - p\right] dv\right] dt$$

$$= \int_{\infty}^{v}\left[t\left(\frac{\partial p}{\partial t}\right)_v - p\right] dv = -\frac{a_1 m_1{}^2 t^2}{(v - B_1 m_1)}\left(\frac{\partial B_1}{\partial t}\right), \tag{61}$$

using equation (VII). Finally the equation for ϵ becomes

$$\epsilon_1 = m_1 \int_{t_0}^{t} c_1{}^* \, dt - \frac{a_1 m_1{}^2 t^2}{v - B_1 m_1} \left(\frac{\partial B_1}{\partial t} \right) + m_1 E_1. \qquad (62)$$

This equation is, as it should be, identical with the energy equation obtained by starting directly with the $\left(\frac{\partial \epsilon}{\partial v}\right)_t$ differential equation.

The entropy may be computed by solving the equations

$$\left(\frac{\partial \eta}{\partial v}\right)_t = \left(\frac{\partial p}{\partial t}\right)_v, \qquad \left(\frac{\partial \eta}{\partial t}\right)_v = \frac{c}{t}. \qquad (63)$$

The entropy expression, using (VII) in connection with the first differential equation becomes, after adding and subtracting $a_1 m_1 \log \frac{v - B_1 m_1}{m_1}$,

$$\begin{aligned}\eta_1 &= m_1 \int_{\infty}^{v} \left(\frac{\partial p}{\partial t}\right)_v dv + m_1 f_1(t) + m_1 H_1 \\ &= \int_{\infty}^{v} \left[\left(\frac{\partial p}{\partial t}\right)_v - \frac{a_1 m_1}{v - B_1 m_1} \right] dv + a_1 m_1 \log \frac{v - B_1 m_1}{m_1} \\ &\qquad + m_1 f_1(t) + m_1 H_1. \qquad (64)\end{aligned}$$

Integration gives finally

$$\eta_1 = m_1 f_1(t) + a_1 m_1 \log \frac{v - B_1 m_1}{m_1} - \frac{a_1 m_1{}^2 t}{(v - B_1 m_1)} \frac{\partial B}{\partial t} + m_1 H_1. \quad (65)$$

Starting with the second differential equation there results, again using (VII),

$$\begin{aligned}\eta_1 &= m_1 \int_{t_0}^{t} \frac{c_1}{t} \, dt + m_1 f_1(v) + m_1 H_1 = m_1 \int_{t_0}^{t} c_1{}^* \frac{dt}{t} \\ &\quad + m_1 \int_{t_0}^{t} \left[\int_{\infty}^{v} t \left(\frac{\partial^2 p}{\partial t^2}\right)_v dv \right] \frac{dt}{t} + m_1 f_1(v) + m_1 H_1 \\ &= m_1 \int_{t_0}^{t} c_1{}^* \frac{dt}{t} + \int_{\infty}^{v} \left[\left(\frac{\partial p}{\partial t}\right)_v - \frac{p}{t} \right] dv + m_1 f_1(v) + m_1 H_1 \\ &= m_1 \int_{t_0}^{t} c_1{}^* \frac{dt}{t} - \frac{a_1 \, m_1{}^2 t}{(v - B_1 m_1)} \frac{\partial B_1}{\partial t} + m_1 f_1(v) + m_1 H_1. \quad (66)\end{aligned}$$

Comparing the two entropy expressions gives for the final entropy equation

$$\eta_1 = m_1 \int_{t_0}^{t} c_1{}^* \frac{dt}{t} + a_1 m_1 \log \frac{v - B_1 m_1}{m_1} - \frac{a_1 m_1{}^2 t}{(v - B_1 m_1)} \frac{\partial B_1}{\partial t} + m_1 H_1. \tag{67}$$

The ζ function $\epsilon_1 + p_1 v_1 - t\eta_1$ may now be formed by substituting the energy and entropy, with the result

$$\zeta_1 = m_1 \int_{t_0} c_1{}^* \, dt + m_1 E_1 + a_1 m_1 t + m_1 B_1 p_1 - m_1 t \int_{t_0}^{t} c^* \frac{dt}{t} - m_1 a_1 t \log \frac{a_1 t}{p_1} - m_1 H_1 t, \tag{68}$$

and for a mixture, employing the rule of Gibbs,

$$\zeta = \sum \zeta_1 = \sum m_1 \int_{t_0}^{t} c_1{}^* \, dt + \sum m_1 E_1 + \sum a_1 m_1 t + \sum m_1 B_1 p_1 - \sum m_1 t \int_{t_0} c_1{}^* \frac{dt}{t} - \sum m_1 a_1 t \log \frac{a_1 t}{p_1} - \sum m_1 H_1 t. \tag{69}$$

The equations for $\mu_1, \mu_2, \ldots$ and $c_1, c_2, \ldots$ can be readily obtained from the last equation by differentiation, i.e.,

$$\mu_1 = \int_{t_0}^{t} c_1{}^* \, dt + E_1 + p_1 B_1 + a_1 t - t \int_{t}^{t} c_1{}^* \frac{dt}{t} - a_1 t \log \frac{a_1 t}{p_1} - H_1 t, \tag{70}$$

$$- t \left[\frac{\partial}{\partial t} \left(\frac{\partial \zeta_1}{\partial t} \right)_p \right]_v = m_1 c_1 = m_1 c_1{}^* + \frac{2 m_1{}^2 \alpha_1 A_1{}^2}{(v - B_1 m_1) a_1 \beta_1 t^2}, \tag{71}$$

using (VIIa) and neglecting higher terms in the reciprocal of

$(v - B_1m_1)$. Equation [280] now becomes

$$c = \sum \left(c^* + \frac{2m_1\alpha_1 A_1^2}{(v - B_1m_1)a_1\beta_1 t^2} \right)$$

$$+ \text{ higher terms in } \frac{1}{t} \text{ and } \frac{1}{v}. \tag{72}$$

19. Ideal Gas Mixture in a Potential Field. The paragraph beginning Gibbs, I, 158, last line, is introduced to emphasize the fact that in a mixture of gases, as in the atmosphere, each gas may be assumed to react to the gravitational field independently of the presence of the other gases[37]. The point is made use of by Lord Rayleigh to investigate the work of separating gas mixtures and the reader is referred to Vol. I p. 242 of *Scientific Papers*, Lord Rayleigh, Camb. Univ. Press, 1899; *Phil. Mag.*, 49, 311, (1875).

20. Vapor Pressure of a Liquid under Pressure from a Neutral Gas. The subject of the effect of an insoluble and neutral gas on the vapor pressure of a liquid has been discussed earlier, making use of [272] in connection with the comments on the additive law of vapor pressures. The treatment taking account of a finite solubility of the neutral gas in the liquid is given in Gibbs, I, beginning p. 160, last paragraph. It will be seen that the phenomena connected with Henry's law constitute a special case of a binary mixture. Thus with carbon dioxide at zero degrees the pressure may be increased to 34.4 atm. at which point carbonic acid would liquefy since this is the saturation pressure. The temperature of the system may also be above the critical temperature of the neutral gas as with carbon dioxide above 31°, and in the process for separating helium from the natural gas in Texas.

The general equations for the case of a two-phase binary mixture are

$$\left.\begin{aligned} -v'\,dp + \eta'\,dt + m_1{}'d\mu_1{}' + m_2{}'d\mu_2{}' &= 0, \\ -v''dp + \eta''dt + m_1''d\mu_1'' + m_2''d\mu_2'' &= 0. \end{aligned}\right\} \tag{73}$$

At equilibrium $d\mu_1' = d\mu_1''$, $d\mu_2' = d\mu_2''$, whence, if $m_2'/m_1' = r'$

and $m_2''/m_1'' = r''$,

$$\left(\frac{v'}{m_2'} - \frac{v''}{m_2''}\right) dp = \left(\frac{\eta'}{m_2'} - \frac{\eta''}{m_2''}\right) dt + \left(\frac{1}{r'} - \frac{1}{r''}\right) d\mu_1', \tag{74}$$

$$\left(\frac{v'}{m_1'} - \frac{v''}{m_1''}\right) dp = \left(\frac{\eta'}{m_1'} - \frac{\eta''}{m_1''}\right) dt + (r' - r'')\, d\mu_2'. \tag{75}$$

When r' is equal to r'' the ratios of the components in both vapor and liquid phases are identical, and the system resembles a pure substance in its thermodynamic behavior (mixture of constant boiling point). To show this, add equations (74) and (75), put $(m_1' + m_2') = M' = 1$, $(m_1'' + m_2'') = M'' = 1$, and since $r' = r''$

$$\left(\frac{1}{m_1'} + \frac{1}{m_2'}\right) = \frac{(1 + r')^2}{r'} = \frac{(1 + r'')^2}{r''} = \left(\frac{1}{m_1''} + \frac{1}{m_2''}\right). \tag{76}$$

There is obtained finally

$$(v' - v'')\frac{dp}{dt} = (\eta' - \eta''). \tag{77}$$

The v' in this formula is the volume of one gram of the vapor mixture in equilibrium with the liquid mixture of constant boiling point t, and v'' the volume of a gram of the latter liquid at t. The heat required to evaporate one gram of the special composition is, therefore,

$$\lambda = t\frac{dp}{dt}(v' - v''). \tag{78}$$

The heat of evaporation generally, and other quantities pertaining to a binary mixture may be obtained from the equations (73) when $d\mu_1'$ and $d\mu_2'$ are known. A convenient transformation of form is the following, whereby the potentials are expressed in terms of the quantities $\mathfrak{a}'$, $\mathfrak{a}''$, dr', and dr''. To carry out the transformation use is made of the following relationships obtained from [92] by cross differentiation, temperature and pressure being kept constant.

$$(a)\qquad \left.\begin{aligned} \left(\frac{\partial \mu_2'}{\partial m_1'}\right)_{p,\,t,\,m_2'} &= \left(\frac{\partial \mu_1'}{\partial m_2'}\right)_{p,\,t,\,m_1'}, \\ \left(\frac{\partial \mu_2''}{\partial m_1''}\right)_{p,\,t,\,m_2''} &= \left(\frac{\partial \mu_1''}{\partial m_2''}\right)_{p,\,t,\,m_1''}. \end{aligned}\right\} \qquad (79)$$

$$(b)\qquad \left.\begin{aligned} \mathfrak{a}' &= -\, m_1' \left(\frac{\partial \mu_2'}{\partial m_1'}\right)_{p,\,t,\,m_2'}, \\ \mathfrak{a}'' &= -\, m_1'' \left(\frac{\partial \mu_2''}{d m_1''}\right)_{p,\,t,\,m_2''}. \end{aligned}\right\} \qquad (80)$$

$$(c)\qquad \left.\begin{aligned} d\mu_1' = d\mu_1'' &= \left(\frac{\partial \mu_1'}{\partial m_1'}\right)_{p,\,t,\,m_2'} dm_1' \\ &\quad + \left(\frac{\partial \mu_1'}{\partial m_2'}\right)_{p,\,t,\,m_1'} dm_2', \\ d\mu_2' = d\mu_2'' &= \left(\frac{\partial \mu_2''}{\partial m_1''}\right)_{p,\,t,\,m_2'} dm_1'' \\ &\quad + \left(\frac{\partial \mu_2''}{\partial m_2''}\right)_{p,\,t,\,m_1'} dm_2''. \end{aligned}\right\} \qquad (81)$$

The following equations may now be written, where λ_1, λ_2 are the quantities of heat required to evaporate a unit quantity of constituent 1 or 2 from the mixture, and $\Delta_1 v$, $\Delta_2 v$ are the corresponding changes in volume of a unit of components 1 or 2 in passing into vapor:

$$\frac{\lambda_1}{t}\, dt = \Delta_1 v dp - \mathfrak{a}' dr' + \mathfrak{a}'' dr'', \qquad (82)$$

$$\frac{\lambda_2}{t}\, dt = \Delta_2 v dp + \mathfrak{a}' \frac{dr'}{r'} - \mathfrak{a}'' \frac{dr''}{r''}. \qquad (83)$$

21. Application to "Gas-Streaming" Method of Measuring Vapor Pressures. An instance of some practical importance in the application of these equations will now be discussed. The determination of vapor pressures by the "streaming method" was referred to earlier in connection with the Poynting effect, but a fuller discussion was postponed until the Gibbs-Dalton rule and some of its consequences were developed. There are essentially three effects which it is necessary to consider in order to use the method for the exact determination of vapor pressures. First, the effect of the pressure of the neutral gas on the vapor pressure of the liquid must be determined. This is the Poynting effect and has already been sufficiently discussed. Second, the depression of the vapor pressure of the liquid due to the dissolved gas must be computed. If, as usual, the solubility is slight, as with water at zero degrees saturated with air at atmospheric pressure, the change in vapor pressure due to solubility is negligible. Third, Dalton's law in the form usually applied, $p_1 = x_1 p$ or $p_1 = \frac{r_1}{\Sigma\, r_1}\, p$ (Gibbs' notation, c.f. [298]), where x is the mol fraction, is inexact. The example to follow will illustrate the use of the Gibbs-Dalton rule, $p = \Sigma p_1$.

The third correction may be made by using the latter rule, or we require actual experimental data relative to the p, v, t behavior for the mixtures of interest and the neutral gas. Equivalent to the latter data is a knowledge of the constants of the equation of state for the two gases (gas emitted by liquid and neutral gas) together with the law of combination of the constants of the equation of state[38] to give the properties of mixtures. Enough knowledge of the latter sort is available to be useful in many cases.

As a concrete problem, suppose an aqueous salt solution at the fixed temperature 21.2° is in equilibrium with nitrogen, the total pressure of the gaseous mixture being one atmosphere. Let the water vapor be absorbed and weighed while the nitrogen is passed along to be measured for pressure and volume at 25°C. The weight of the water is 0.45 gram or 0.02498 mols, and the nitrogen has a volume of 24000 c.c. at 1 atm., or 0.98111 mols. The perfect gas law is suitable for computing the latter since nitrogen is very nearly a perfect gas at 25° and 1 atm. The constants β and A of the equation of state (VIIa) for water and nitrogen* are

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* The constants given for water are only approximate. Those for nitrogen are valid for low pressures at ordinary temperatures. This is not the place for a complete and exact exposition of the theory of reduc-

$$\beta_{H_2O} = 81, \qquad A_{H_2O} = 57 \times 10^6,$$

$$\beta_{N_2} = 47.6, \qquad A_{N_2} = 1.255 \times 10^6,$$

the units being c.c. per mol and atmospheres. Using the Gibbs-Dalton rule that the total pressure is equal to the sum of the pressures which each of the separate gases would manifest if alone present in the total volume of the mixture we find

$$p = \frac{82.06 \times 294.3 \times 0.02482}{V + 56.6} + \frac{82.06 \times 294.3 \times 0.97516}{V + 4.2}.$$

A few trials will be found to give 24144.4 c.c. as the volume for the pressure of one atmosphere. The first term of the right hand side becomes 0.02477 and the second 0.97523. But these terms are the equilibrium pressures according to the Gibbs-Dalton rule and hence the pressure of the water vapor is 18.825 mm. The application of the Dalton rule as usually applied ($p_1 = px_1$) gives on the other hand 18.866 mm.; a difference of one part in 460. The actual vapor pressure of the solution is 18.820 mm.

A similar computation may be made using the fugacity function[39, 40, 41, 42]. In the latter case the equilibrium fugacity, as proposed by Lewis and Randall, is given by the rule $f_e = f_p x_1$, where f_p is the fugacity of the gas of interest at the pressure p of the mixture.

Finally the equilibrium pressure may be computed using the equation of state constants for the gases of interest and computing the equation of state constants for the mixtures by combination rules for the constants known to hold for mixtures of nitrogen and methane[38]. The latter method has met with success in a number of applications.

22. Heat of Evaporation of a Liquid under Constant Pressure. The discussion (Gibbs, I) beginning at the bottom of page 161 and continuing to the top of page 163 contains an elegant proof of the impossibility of an uncompensated change in

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ing "gas-current" observations, especially since the procedure has been given in detail recently by H. T. Gerry and L. J. Gillespie (*Phys. Rev.*, **40**, 269 (1932)) for the case of the vapor pressures of iodine.

vapor pressure when the emitting solid or liquid is compressed. It will be recognized that the proof depends on the use of [272] by which the change in vapor pressure with pressure on the liquid or solid phases was computed. It may be well to remark that the energy equation corresponding to this case may be easily deduced from the general equations (73) applied to one component. Thus,

$$\left.\begin{aligned} v'\,dp &= \eta'\,dt + m_1'\,d\mu_1', \\ v''dP &= \eta''dt + m_1''d\mu_1''. \end{aligned}\right\} \tag{84}$$

Here dp refers to the vapor pressure change of the pure substance (single accent), but if the pressure P is maintained constant on the liquid phase and equilibrium subsists we have

$$(\eta' - \eta'') = \frac{dp}{dt}\,v'$$

or

$$\lambda_P = t\,\frac{dp}{dt}\,v'. \tag{85}$$

The latent heat of evaporation under conditions of constant pressure on the liquid phase accordingly differs from the normal heat under saturation conditions.

In a similar manner if a pressure P is applied to the solid phase but not the liquid phase we find

$$\lambda_P = t\,\frac{dp}{dt}\,v'', \tag{86}$$

where v'' is the volume of the liquid. Evidently $\frac{dt}{dp}$, the change in melting point with pressure, will be large compared with the ordinary change of melting point with pressure where the same pressure is applied to both phases. The equation aids incidentally in understanding the extruding of metals, made possible no doubt because of actual instantaneous creation of liquid phases under the enormous pressures applied to the solid.

23. Fundamental Equations from Gibbs-Dalton Law. The fundamental equations in the form given in [291], [292] and [293] are easily obtained. The latter equation may also, however, be expressed in the form:

$$\zeta = \sum [m_1E_1 + m_1t(c_1 + a_1 - H_1)] - \sum c_1m_1t \log t - \sum a_1m_1t \log \frac{a_1t}{px_1}, \qquad (87)\ [293]$$

where x_1, the mol fraction, is equal to $\frac{a_1 m_1}{\Sigma a_1m_1}$. The content of the paragraph following [293] should be carefully noted.

24. Case of Gas Mixtures Whose Components are Chemically Reactive. Thus far only gas mixtures with independently variable components have been considered. The material following [293] (Gibbs, I, 163) therefore emphasizes the distinction which must be made between gas mixtures of the former kind, and those with convertible or chemically reactive components. The characteristic of the latter is of course that chemical changes proceed by whole numbers or fixed ratios. Two molecules of hydrogen always require one molecule of oxygen, never more nor less, to form one molecule of water, and three molecules disappear when two water molecules are formed. As a consequence we need only be concerned, in our equations of thermodynamics for chemically combining gases, with these whole number ratios and not with actual masses. Thus it is clear that, in so far as convenience is served, our equations for gas mixtures could be expressed in units of mass proportional to the masses of the molecules of the separate and distinct chemical species. This, of course, is the almost universal custom in chemistry at present, and in all the preceding formulae it is merely required that n, the number of mols, be substituted for m the masses. The constants $a_1, a_2, \ldots$ must also be expressed in terms of the mol as the unit of mass. Thus (87) [293] would be written

$$\zeta = \sum n_1 \Big[E_1 + t(c_1 + R - H_1) \Big] - \sum n_1c_1t \log t - \sum n_1Rt \log \frac{Rt}{px_1}, \qquad (88)\ [293]$$

where R, the universal gas constant, is equal to the product of a_1, a_2, . . . and the corresponding molecular weights. Here E_1, c_1 and H_1 are also assumed to have been multiplied by the corresponding molecular weights.

II. Inferences in Regard to the Potentials in Liquids and Solids (*Gibbs, I, 164, 165*)

There might be included under this heading a large portion of the principles and doctrine which have found application in physical chemistry in the last half-century. The fact that a comparatively simple basis of fact could have such general applicability was well known to Gibbs, as is indicated by the last sentence of the section (7th line from bottom, p. 165). Indeed a few empirically discovered facts interrelated thermodynamically suffice to form the theory of those liquid mixtures wherein the masses of one or several constituents are very small relative to the mass of one of the components[43]. The principle of the equality of the potentials of a component in equilibrium in the coexisting gaseous and liquid or solid phases affords the means of determining the potentials of the condensed phases. Because of this a full knowledge of the properties of pure gases and their mixtures is of fundamental importance in extending the range of applicability of the general theory. Thus it becomes clear that great importance attaches to a knowledge of the constants of the equation of state for different substances, and the rules for combining these constants, in order that the constants for the equations for mixtures may become available. On the other hand[51] given sufficient data for pure substances and their mixtures, the required thermodynamic quantities may be accurately computed empirically, using the assumption that the ideal gas laws hold rigorously in the limit of low pressures. It is evident, however, that on this basis an almost prohibitive amount of experimental data would be required to satisfy the needs of the science, and therefore continuous effort should be made to develop a rational form of equation of state with the aid of statistical mechanics. It is, indeed, apropos to add that the correlations of physico-chemical facts by thermodynamics can receive much independent assistance and support from the theorems and results deducible from statistical mechanics. It is also evident of course that, outside of the field of equilibrium states, thermodynamics is of no service and progress in the theory of non-equilibrium states depends on the perfection of statistical theory. Modern atomic and molecular theories likewise have an important part to play in leading to an improved knowledge of molecular constants and molecular encounters, which is indispensable to the future progress of physical chemistry.

25. Henry's Law. The law that the concentration of the dissolved constituent is proportional to the pressure of the gaseous constituent is to be regarded as applying strictly only in the limit where the amount of dissolved gas is vanishingly small. The deviation in the case of carbon dioxide and water, for example, where it amounts over the interval 30 atm. to 37 percent at zero degrees and 29 percent at 12.43 degrees[44] is typical. The pressure of the gas phase, in this case, increases more rapidly than the amount of gas dissolved.

By way of accounting for the deviations from Henry's law it may be noted that the gaseous mixture over a liquid is now known to be far from a perfect gas. This particular aspect of the problem has received recent attention, and the changes in volume on formation of the mixture, together with the significant thermodynamic formulae, have been developed[45, 46, 9] using the fugacity function introduced by G. N. Lewis[47, 48, 49, 50, 9]. This convenient function in the case of a pure gas is related to the μ function of Gibbs as follows:

$$f = p\, exp. \left[\frac{1}{a_1 t}(\mu - \mu_i)\right], \tag{89}$$

where μ is the potential at pressure p and temperature t, and μ_i is the potential at the same pressure and temperature assuming the ideal gas laws to hold. From the equation it is evident that $f \rightarrow p$ in the limit when the pressure approaches zero. The equilibrium fugacity, f_e, of one of the gases, 1, in a mixture of gases, is given by the equation[51, 52]

$$f_e = p x_1\, exp. \left[\frac{1}{a_1 t}\int_0^p \left(\bar{v}_1 - \frac{a_1 t}{p}\right) dp\right], \tag{90}$$

where $\bar{v}_1$ is the partial volume $\left(\frac{\partial v}{\partial m_1}\right)_{p,\,t,\,m} = \left(\frac{\partial \mu}{\partial p}\right)_{t,\,m}$, and x_1 the mol fraction. The analogue of Henry's law in terms of fugacity becomes for dilute solutions $f_e = km_1''$, where m_1'' is the mass of the dissolved gas in the liquid phase. A glance at the expression above for f_e makes evident that a part of the deviations from Henry's law will be found in the failure of the equilibrium gas mixture to conform to the ideal gas laws.

26. Raoult's Law of Vapor Pressure and the Thermodynamic Theory of Dilute Solutions. Another principle in the same class with Henry's law is Raoult's law, according to which the ratio of the vapor pressure of a solution to the normal saturation pressure is equal to the ratio of the number of molecules of the solvent to the sum of those of the dissolved substance and the solvent. Designate the salt with subscript 2 and the solvent with subscript s.

$$\left.\begin{aligned} \frac{p}{p_{sat.}} &= \frac{n_s}{n_s + n_2}, \\ \text{or} \qquad \frac{p_{sat.} - p}{p_{sat.}} &= \frac{n_2}{n_s + n_2}, \\ \frac{p_{sat.} - p}{p} &= \frac{n_2}{n_s}. \end{aligned}\right\} \tag{91}$$

The relation of this result to the general Gibbs theory is easily established for dilute salt solutions. A salt solution may be regarded as a special case of a binary mixture in which the component in smallest amount is non-volatile. The second of the pair of equations in a, equation (83), vanishes and there remains, since $m_2' = 0$,

$$\frac{\lambda_1}{t} = \Delta_1 v \frac{dp}{dt} + \mathfrak{a}'' \frac{dr''}{dt}. \tag{92}$$

Note in the first place that if $m_2''/m_1'' = r''$ is constant, and we let

$$\lambda_0 = t \frac{dp_0}{dt} (v_1 - v_2)$$

represent the heat of vaporization of the pure solvent, the heat of dilution is obtained at once for the case where the vapor, of volume v_1, may be taken to be an ideal gas, and the liquid volume v_2 is negligible. We find

$$\lambda_1 - \lambda_0 = \Delta\lambda = a_s m_s t^2 \left(\frac{\partial \log p/p_0}{\partial t}\right)_{r''}. \tag{93}$$

Taking the temperature as constant in the general equation, assuming that $v = \dfrac{a_s m_s' t}{p}$ (m_s' is the mass of vapor of solvent), we drop the accent in $\mathfrak{a}''$ and r''. This gives

$$\frac{dp}{dr} = -\frac{\mathfrak{a}}{\Delta_1 v} = -\frac{\mathfrak{a}}{a_s m_s' t}\,p. \tag{94}$$

Integrating the last equation there is obtained

$$\int_{p_{sat.}}^{p} \frac{dp}{p} = \log\frac{p}{p_{sat.}} = -\frac{\mathfrak{a}}{a_s m_s' t}\,r. \tag{95}$$

But $p_{sat.} - p$ may be put equal to Δp, and m_s' may be taken to be numerically equal to M_s' the molecular weight of the vapor, whence

$$\frac{\Delta p}{p_{sat.}} = \frac{\mathfrak{a}}{Rt}\frac{m_2}{m_s}. \tag{96}$$

Raoult's law in dilute solution may be expressed in the form $\Delta p/p_s = n_2/n_s$ when n_2 is small relative to n_s. By comparison we find

$$\mathfrak{a} = -m_s\left(\frac{\partial \mu_2}{\partial m_s}\right)_{p,\,t,\,m_2} = Rt\frac{M_s}{M_2},$$

which is constant at constant temperature and depends only on the molecular weight ratio $\dfrac{M_s}{M_2}$. Finally we obtain

$$\mu_2 = -\frac{M_s}{M_2} Rt \log m_s + f(p, t, m_2)$$

for the relation between μ_2 and the masses of solvent and dissolved substance.

Again for constant pressure there is obtained from the general equation

$$\left(\frac{dt}{dr}\right)_p = \frac{t\,a}{\lambda_1}^{*}. \tag{97}$$

From the previous inference it is clear that a is a positive quantity, hence dr and dt change in the same sense or for increased concentration there is a proportionate rise in temperature. Inserting the value of a found in the preceding paragraph we find on integrating:

$$t - t_0 = \frac{Rt_0t}{\lambda_1}\frac{n_2}{n_s}, \tag{98}$$

which is the usual equation for the elevation of the boiling point. A similar equation of corresponding form gives the depression of the freezing point for dilute solutions.

If λ_1 is assumed given by $[\lambda_0 + ct]$, we obtain

$$\lambda_0\frac{t - t_0}{t_0t} + c\log\frac{t}{t_0} = R\frac{n_2}{n_s}. \tag{99}$$

Expanding $\log t/t_0$ in a series of powers of $\dfrac{t - t_0}{t_0}$ leads, as a first approximation, to equation (98); retaining however the second term leads to the equation

$$t - t_0 = \frac{Rt_0t}{\lambda_0}\cdot\frac{n_2}{n_s}\left[1 - \frac{ct_0}{\lambda_0}\right]. \tag{100}$$

From the foregoing discussion the nature of the deficiencies in the formulae arising from the approximations used will be clear. A more complete theory may be constructed in various ways, but up to the present time no very systematic coördination of the theoretical development and exact experimentation has been undertaken. Recently a method has been discussed by G. van Lerberghe[53] which has as a basis the development of the function $p = f(t_1, v_1, m_1, m_2, \ldots)$ by Taylor's theorem. That it is possible to develop a consistent and rational system for the discussion of the properties of solutions on such a basis has, in fact, been pointed out by Planck[54]. The method is equivalent in some respects to the system of treating solutions developed by G. N. Lewis and systematically presented by Lewis and Randall in their *Thermodynamics*.

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* Note that λ_1 is the heat required to remove unit mass of solvent vapor from the salt solution. We may assume that λ_1 is equal to the heat of evaporation of the pure solvent, or better, that it is a function of temperature of the form $[\lambda_1 = \lambda_0 + c_1t]$, where c_1 is a constant.

Methods of treating solutions along these lines have, however, the limitations of procedures whose foundation is entirely empirical. On the other hand any other procedure requires much detailed knowledge pertaining to molecular interaction and the surmounting of formidable mathematical difficulties[55]. Although the initial steps have been taken in acquiring the requisite knowledge of the attractive and repulsive fields of molecules, very much ground remains to be won before a complete molecular statistical theory of solutions can be achieved. The mathematical difficulties, forming an important part of the problem, remain at the moment practically unsolved[56] except for the case of infinitely dilute solutions[57]. The case of electrolytes at infinite dilution has been treated by Debye and Hückel[58, 59], and the accord of their theory with the facts is astonishingly good in spite of important fundamental limitations.

III. Considerations Relating to the Increase of Entropy Due to the Mixture of Gases by Diffusion (*Gibbs, I, 165–168*)

The entropy change on mixing gases has already been mentioned with reference to the difference in entropy which arises when pure gases mix at temperature, t, and constant pressure, p. Thus we may imagine two perfect gases 1 and 2, contained in the apparatus indicated in the diagram, Fig. 1.

Suppose that the pistons are permeable to the gases as indicated and the usual assumptions made with regard to the absence of frictional effects. Each gas is assumed to occupy its portion of the cylinder at the same pressure and temperature when the pistons are in contact. As the pistons are slowly moved out each gas passes through its respective semi-permeable membrane into the space between the pistons, constituting finally a mixture of the two gases originally in the pure state. By moving the pistons together the separation can be effected. With the gases in the pure state we have,

$$\left.\begin{aligned}\eta_1 &= m_1c_1 \log t + m_1a_1 \log \frac{V_1}{m_1} + m_1H_1,\\ \eta_2 &= m_2c_2 \log t + m_2a_2 \log \frac{V_2}{m_2} + m_2H_2.\end{aligned}\right\} \quad (101)\ [278]$$

But $\dfrac{a_1m_1t}{p} = V_1$ and $\dfrac{a_2m_2t}{p} = V_2$, while $a_1m_1 + a_2m_2 = (V_1 + V_2)\dfrac{p}{t} = \dfrac{pV}{t}$, and after mixing each gas will occupy the total volume $V = V_1 + V_2$, or

$$\left.\begin{aligned}\eta_1' &= m_1c_1 \log t + m_1a_1 \log \frac{V}{m_1} + m_1H_1,\\ \eta_2' &= m_2c_2 \log t + m_2a_2 \log \frac{V}{m_2} + m_2H_2.\end{aligned}\right\} \quad (102)$$

The difference between the respective entropies after and before mixing is given, therefore, by the following equations:

$$\left.\begin{aligned}\eta_1' - \eta_1 &= -m_1a_1 \log \frac{V_1}{V} = -m_1a_1 \log \frac{a_1m_1}{a_1m_1 + a_2m_2},\\ \eta_2' - \eta_2 &= -m_2a_2 \log \frac{V_2}{V} = -m_2a_2 \log \frac{a_2m_2}{a_1m_1 + a_2m_2},\end{aligned}\right\} \quad (103)$$

since $V_1/V = \dfrac{a_1m_1}{a_1m_1 + a_2m_2}$ and $V_2/V = \dfrac{a_2m_2}{a_1m_1 + a_2m_2}$ by the relations following (101) [278] above.

Each difference is positive since the mol fractions are necessarily each less than unity, and therefore an increase of entropy has attended the mixing. If each gas is present in equal amount the total increase becomes

$$(a_1m_1 + a_2m_2) \log 2 = \frac{pV}{t} \log 2. \qquad (104)\ [297]$$

The generalization of the above result follows easily, and if $x_1, x_2, \ldots x_i$ are the mol fractions we find

$$\sum_1^i (\eta_1' - \eta_1) = \sum_1^i a_1 m_1 \log \frac{1}{x_1} = C^{-1} \sum_1^i r_1 \log \frac{\Sigma r_1}{r_1}, \qquad (105)\ [298]$$

where C^{-1} in Gibbs' notation is equal to the universal gas constant, usually designated by R. The discussion following equation [297] is too complete to require comment other than to draw attention to the remark which admirably sums up the import of the Gibbs theorem on entropies: "the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability" (15th line from bottom p. 167). It is of additional interest to note that an entirely analogous theorem may be deduced by starting with equation [92] of Gibbs' *Statistical Mechanics* (Gibbs, II, Part I, 33) and extending the equation to include two or more molecular species.

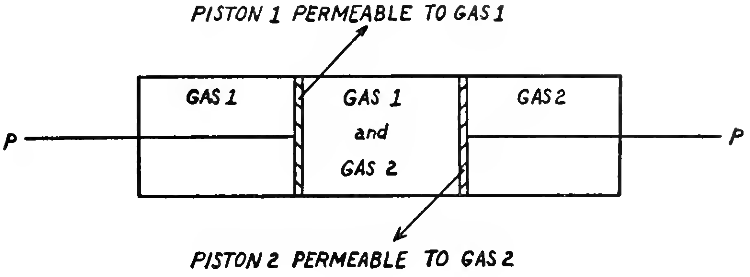

FIG. 1

IV. The Phases of Dissipated Energy of an Ideal Gas Mixture with Components Which Are Chemically Related

(*Gibbs, I, 168–172*)

Before reading this section, the section on "Certain Points relating to the Molecular Constitution of Bodies," pp. 138–144, should be consulted. The immediate goal is to provide the basis for treating the phenomena exhibited by mixtures of gases which are capable of chemical interaction. What is sought is a scheme whereby the equilibrium amounts of the different distinct molecular species may be correlated as a function of the energy of interaction, the pressure or volume, and the temperature. At least this is the goal which is of chief interest to the chemist using thermodynamics as a means of correlating equilibrium data, and some conceptions of a molecular nature are required in practice notwithstanding the often repeated statement that thermodynamics has no need of molecular hypotheses. The latter dictum is really true only in a restricted sense in the field of the applications of thermodynamics to the extensive and varied phenomena of chemistry.

The term *phases of dissipated energy* may be assumed equivalent to what is now generally called the equilibrium state. It is for this state alone that the energy is a minimum and the entropy a maximum (see Gibbs, I, 56, "Criteria of Equilibrium and Stability"). Of course equilibrium states are not always easy to realize, but in every case of doubt as to the establishment of equilibrium in the case of chemically interacting components the usual test in practice is to vary the independent variables, pressures or temperature or both, at the supposed state of equilibrium and to observe the displacement, finally verifying the possibility of reproducing the original condition of true equilibrium at the point in question.

Gibbs' treatment involves the masses of the components instead of the mols now used. Equation [299] in the concrete case of the formation of water from the elements would be written,

$$1\ g.\ (H_2O) = 8/9\ g.\ (O_2) + 1/9\ g.\ (H_2). \qquad (106)\ [299]$$

But for the condition of equilibrium it has been proved that

$$\Sigma\mu_1\delta m_1 \geqq 0,$$

and our knowledge of the principles of chemical combination allows us to identify the variations δm_1, δm_2, . . . as proportional to the λ coefficients as in (106) [299]. In equation [300], δm_3 may be replaced by -1 if water is assumed to disappear in the reaction, whence δm_2 becomes 8/9 and δm_1 1/9, both reckoned plus, i.e.,

$$\frac{1}{9}\mu_1 + \frac{8}{9}\mu_2 = \mu_3, \qquad (107)\ [301]$$

In terms of v and t as independent variables [276] gives

$$\frac{1}{9} a_1 \log \frac{m_1}{v} + \frac{8}{9} a_2 \log \frac{m_2}{v} - a_3 \log \frac{m_3}{v} \qquad (108)\ ]302]$$

$$= A + B \log t - c/t,$$

in which the values of A, B and C are given by [303], [304], [305].

The mass law is contained in the left-hand member of (108) [302]. For, on multiplying and dividing each term by the respective molecular weights, there results

$$R\left(\frac{1}{9M_1} \log \frac{m_1}{v} + \frac{8}{9M_2} \log \frac{m_2}{v} - \frac{1}{M_3} \log \frac{m_3}{v}\right). \qquad (109)$$

Multiplying and dividing the bracketed member by $M_3 = 18$, and taking $M_1 = 2$, $M_2 = 32$, gives

$$\frac{R}{18}\left[\log \frac{m_1}{v} + \frac{1}{2} \log \frac{m_2}{v} - \log \frac{m_3}{v}\right], \qquad (110)$$

but $\frac{m_1}{v}$, etc., become $\frac{x_1p}{a_1t}, \frac{x_2p}{a_2t}, \frac{x_3p}{a_3t}$. Using Dalton's law of partial pressures in its usual form $p_1 = px_1$, we find

$$\frac{R}{18}\left[\log \frac{p_1 \cdot p_2^{1/2}}{p_3} - \log \frac{a_3}{a_1a_2^{1/2}} - \frac{1}{2} \log t\right]. \qquad (111)$$

The term in the partial pressures is the usual mass law expression, or K_p as the quantity is commonly designated, while the remaining term in the a's is a constant. The case where $\beta_1 + \beta_2 - 1$ is zero corresponds to the case where the sum of the exponents of the partial pressures vanishes. An example exists in the case of the union of H_2 and I_2 to form 2HI, where the total pressure does not enter the reaction equation.

27. Restatement of the Above in Different Notation. Employing mols as the unit of mass, and recognizing from the foregoing that the variations of mass $\delta m_1, \delta m_2, \ldots$ need only be considered as ratios equal in value to the coefficients in the chemical reaction, we write [300] as

$$\Sigma \mu_1 \nu_1 \geqq 0, \qquad (112)\ [300]$$

where ν represents the coefficients, for example -1, $1/2$ and 1 in the decomposition of water. Here the minus sign signifies that a component vanishes while the positive sign signifies the appearance of components formed from those having the minus sign. Assume also that the heat capacities $c_1, c_2, \ldots$ are not constants but functions of the temperature. Starting with equations [265] and [283] there is finally obtained

$$\sum \zeta_1 = \sum n_1 \int_{t_0}^{t} c_1^* dt + \sum n_1 E_1 + \sum n_1 Rt - \sum n_1 t \int_{t_0}^{t} c_1^* \frac{dt}{t} - \sum n_1 Rt \log \frac{Rt}{px_1} - \sum n_1 t H_1,$$

whence

$$\mu_1 = \int_{t_0}^{t} c_1^* dt + E_1 - t \int_{t_0}^{t} c^* \frac{dt}{t} - Rt \log \frac{Rt}{px_1} + Rt - H_1 t. \quad (113)$$

The equivalent of equation (2) [300] may now be easily formed, and on rearrangement there results

$$\sum \nu_1 \log px_1 = -\frac{\sum \nu_1 E_1}{Rt} + \sum \nu_1 \log Rt - \frac{\sum \nu_1 \int_{t_0}^{t} c_1^* dt}{Rt} + \frac{\sum \nu_1 \int_{t_0}^{t} c_1^* dt/t}{R} + \frac{\sum \nu_1 H_1 - \sum \nu_1 R}{R}. \quad (114)\ [309]$$

This equation is perfectly general within the limits of applicability of the perfect gas laws, and [282] and [283] apply. The energy constants and the entropy constants may be adjusted to suit practical convenience, but this has already been referred to earlier and need not detain us here.

The case of the dissociation of water vapor and of the decomposition of hydriodic acid will illustrate in detail the points raised by Gibbs. For the former we have

$$\left.\begin{array}{lll} H_2O = \frac{1}{2} O_2 + H_2, & & \\ \nu_3 = -1, & \nu_2 = \frac{1}{2}, & \nu_1 = 1. \end{array}\right\} \quad (115)$$

In general the heat capacities are known over a limited range of temperature, for H_2 is the only gas whose heat capacity is known at low temperatures. The question of whether the heat capacity approaches 3/2 R or vanishes at zero Kelvin is, moreover, not yet settled. In the case of water vapor values of c_3 are available to temperatures where water vapor is detectably dissociated. Such values must, however, be corrected for heat absorbed due to dissociation; a correction evidently impossible to obtain until the dissociation data can be correlated, and then a final and exact result is only possible by successive approximation. Above zero degrees the heat capacities of most gases increase rather slowly, and in the absence of a generally applicable theory of heat capacities of gases linear expressions, or at most quadratic expansions, may be used. On this basis the heat capacity terms become, when the linear form is used,

$$\sum \nu_1 \int_{t_0}^{t} c_1^{*}dt = \sum \nu_1 a_1 (t - t_0) + \sum \frac{\nu_1 b_1}{2} (t^2 - t_0^2), \qquad (116)$$

$$\sum \nu_1 \int_{t_0} c_1^{*}dt/t = \sum \nu_1 a_1 \log (t/t_0) + \sum \nu_1 b_1 (t - t_0). \qquad (117)$$

The present custom is often to integrate the linear terms between zero Kelvin and t, but such practice, as is frequently the case, had its origin in the earlier erroneous belief that the heat capacity dependence on temperature was as simple below the ice point as it appeared to be above. Note should be taken also of Gibbs' decision to express the reaction pressure-temperature function in terms of the energy constant E_1, a choice very likely induced by the somewhat simpler treatment possible when non-ideal gases are involved.

When $\Sigma\nu_1$ vanishes in (114) [309] the mol fraction function $\Sigma\nu_1 \log x_1$ becomes a function of temperature alone, and thus pressure is without influence on the numbers of the different kinds of molecules so long as the gases are ideal. A further simplification would result if the terms

$$\sum \nu_1 \int_{t_0}^{t} c_1^{*}dt \quad \text{and} \quad \sum \nu_1 \int_{t_0}^{t} c_1^{*}dt/t$$

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vanished, and this assumption is sometimes made when, as is often the case, there is a practically complete lack of heat capacity data. The leading term is of course $\Sigma\nu E_1/Rt$ and is very large in the usual case of gas reactions.

The equation (114) [309] contains the generalization set forth in equations [311] to [318]. It includes also the case referred to in the sentence following [318]; "graded" dissociation illustrated by the reaction $HI \rightarrow H_2 + I_2 \rightarrow 2H + 2I$. It is clear also that the presence of a neutral gas in the reaction mixture is without influence on the value of the equilibrium constant (114) [309] provided p is understood to be the total pressure diminished by the pressure the neutral gas would exert if it alone occupied the volume of the mixture. The influence of a gravitational field of the magnitude available on the earth is exceedingly small and equation [234], Gibbs, I, 146 provides the basis for investigating such effects.

V. Gas Mixtures with Convertible Components

(Gibbs, I, 172–184)

The equation (114) [309] of the previous section includes the case of interest here developed. The term convertible components refers to the formation of multiple molecules such as $(NO_2)_2$; a case which would also be included under the term reversible polymerization or association. The painstaking justification of the application of the principles established for the treatment of mixtures of chemically related components to the present case may seem unnecessary. On the other hand it should be recalled that one of the former axioms of chemistry was that substances of the same qualitative and quantitative composition must possess the same physical properties. Reference may be made to Liebig's discovery of the identity of composition of silver fulminate and silver cyanate as the first definite fact invalidating the axiom. Had NO_2 been colorless the explanation of the considerable change in density of the gas with pressure would probably not have been ascribed to association and dissociation for a long time. As a matter of fact it was the change in color on change of pressure and temperature which prompted the supposition of a change in molecular species, and the measurements of density were then used as confirmatory evidence to establish the fact of the conversion of NO_2 into colorless N_2O_4 as the pressure increased or the temperature diminished.

The assumption has often been made that the departure of gases from the ideal state is to be ascribed generally to the tendency to polymerization. The same idea appeared later in modified form in the attempt to explain all departures from Van der Waals' equation as due to an association collapse of the molecular system, and again in the idea that the formation of the liquid phase was conditioned upon such a collapse. It is clear however that a distinct molecular species of the associated type such as $(NO_2)_2$ occurs comparatively rarely, and that the formation of the liquid phase and the departure of gases from the ideal state must in general be ascribed to quite different causes.

The case of convertible components offers one point of contrast with that of chemically related components, for the latter is as a rule subject to passive resistance (Gibbs, I, 58) whereas the former appears not to be limited in the rapidity with which the ratio of the molecular species can adjust itself to follow the fluctuations of pressure and temperature.[60]

The test, that equation [309] be applicable to the case of convertible components, rests on its successful application in interpreting the densities of N_2O_4 observed under various conditions of temperature and pressure. Admittedly the dissociation of the latter substance into two molecules, and similar chemical reactions, form ideal examples to which the thermodynamic principles of chemical interaction may be expected to apply. Reactions of this class in the gaseous phase appear to be free from the effects of passive resistance and are subject unquestionably to the conditions of equilibrium discussed by Gibbs from page 56 on. They present a problem exemplifying a wide range of the interpretative possibilities latent in thermodynamics.

Evidently it is difficult to provide specific heat data to use in the reaction equation (114) [309] since the freedom of convertibility of the simple and complex molecules cannot be arrested. The apparent heat capacity of the gas mixture will therefore consist of the sum of the heat capacities of quantities of the NO_2 and N_2O_4 molecules dependent on the temperature and pressure and on the heat absorbed in the shift of the molecular species while the mixture is being changed in temperature. An exact knowledge of the ratio of the number of mols of NO_2 and N_2O_4 as a function of temperature and pressure would of course enable such apparent heat capacities to be operated upon with a view to extracting the heat capacities of the separate molecular species, but it is quite impossible to evaluate the terms of equation (114) [309], for example, without the heat capacity data. It might be supposed that (114) [309] could be evaluated omitting the heat capacity terms as a first approximation, and that with such a provisional relation between the amounts of NO_2 to N_2O_4 as a function of p and t one could treat the apparent heat capacity data. The provisional values of the heat capacities could then be used to secure a second approximation of the reaction equation, and this in turn would permit a further refinement in computing the true heat capacities. But this tedious process could not lead to an exact result since in the treatment the perfect gas laws would be involved. Of course, sufficiently precise measurements of the actual density of the mixture would conceivably permit a semi-empirical formulation with (114) [309] as a basis, provided the composition of the mixture could be exactly determined. This is, however, a matter of the greatest difficulty because of the great reaction mobility so that, generally considered, the exact interpretation of density data for mutually convertible components in terms of the numbers of the reacting molecules, the pressure and the temperature, must be admitted to be surrounded with difficulties.

We proceed with the application of equation (114) [309] by omitting all the heat capacity terms and writing for $\Sigma\nu_1 E_1$ ΔE, and for $\dfrac{\Sigma\nu_1 H_1 - \Sigma\nu_1 R}{R}$ the symbol I, giving

$$\log \frac{p}{Rt}\frac{x^2_{\mathrm{NO_2}}}{x_{\mathrm{N_2O}}} = -\frac{\Delta E}{Rt} + I. \qquad (118)\ [309]$$

This is the form adopted by Gibbs.* We proceed to examine a few properties of this equation.

The equation of state of the gas mixture is assumed to be $pv = Rt(n_1 + n_2)$, where n_1 is the number of mols of NO_2 and n_2 the number of N_2O_4, which permits the equation to be expressed as

$$\log \frac{n_1^2}{n_2 v} = -\frac{\Delta E}{Rt} + I. \qquad (119)\ [309]$$

Setting $p\,\frac{x_1^2}{x_2}$ equal to k_p, and $\frac{n_1^2}{n_2 v}$ equal to k_c, and differentiating (118) [309] with respect to t at constant pressure gives the equation

$$\left(\frac{\partial \log k_p}{\partial t}\right)_p = \frac{\Delta E + Rt}{Rt^2}. \qquad (120)$$

But equation [89] on differentiation and substitution of

$$t\left(\frac{\partial \eta}{dp}\right)_t dp + t\left(\frac{\partial \eta}{\partial t}\right)_p dt \quad \text{or} \quad - t\left(\frac{\partial v}{\partial t}\right)_p dp + c_p dt \quad \text{for } d\epsilon + p dv,$$

where c_p is the heat capacity at constant pressure, gives

$$d\chi = c_p dt - \left[t\left(\frac{\partial v}{\partial t}\right)_p - v\right] dp, \qquad (121)$$

and

$$\left(\frac{\partial \chi}{\partial t}\right)_p = c_p, \quad \left(\frac{\partial \chi}{\partial p}\right)_t = -\left[t\left(\frac{\partial v}{\partial t}\right)_p - v\right] = \left(\frac{\partial v \tau}{\partial \tau}\right)_p, \qquad (122)$$

where $\tau = t^{-1}$. The summation principle [283] leads to the conclusion, however, using the first of the above pair of equations, that

$$\chi = [\Sigma\, \nu_1 \chi_1 + \Sigma\, \nu_1 c_{p_1} dt]_p. \qquad (123)$$

In (118) [309] the heat capacity terms have been assumed to vanish, and application of the same condition to the last equation leads to

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* See paragraph beginning line 4, Gibbs, I, 180.

$$\chi = \Sigma\nu_1\chi = \Delta\chi_1 = \Delta E + \Sigma\nu_1 Rt = \Delta E + Rt. \qquad (124)$$

But this is the numerator of the expression (120) for the derivative with respect to t of log k_p, which is to be identified as the heat of reaction at constant pressure subject to the condition that the specific heat capacities of the reacting gases are all equal (i.e., $\Sigma\nu_1 c_1 = 0$).

The temperature derivative of log k_c, taken for constant volume, is

$$\left(\frac{\partial \log k_c}{\partial t}\right)_v = \frac{\Delta E}{Rt^2}, \qquad (125)$$

and ΔE is the heat of reaction at constant volume. From [86] we find $\left(\frac{\partial \epsilon}{\partial t}\right)_v = c$ and integrating at constant volume using [283] we have

$$\epsilon = \left[\Delta E + \int_{t_0}^{t} \sum \nu_1 c_1 dt\right]_v, \qquad (126)$$

which is the general equation for the energy at constant volume.

The above is the equivalent, with some elaboration of detail, of the material of Gibbs, I, 180 and the first third of 181. It remains to note that since we have defined log k_p and log k_c as equal to $\sum \nu_1 \log px_1$ and $\sum \nu_1 \log \frac{x_1}{v}$, $\left(\frac{\partial \log k_p}{\partial p}\right)_t$ is zero and

$$\left(\frac{\partial \log k_c}{\partial v}\right)_t = 0$$

from (114) [309]. If, however, we set $\Sigma\, \nu_1 \log x_1$ equal to log k_x, then from (114) [309] it follows that

$$\left(\frac{\partial \log k_x}{\partial p}\right)_t = -\frac{\Sigma\, \nu_1}{p}, \qquad (127)$$

$$\left(\frac{\partial \log k_x}{\partial v}\right)_t = \frac{\Sigma\, \nu_1}{v}. \qquad (128)$$

31. A More General Application of the Gibbs-Dalton Rule. A more general reaction equation than (114) [309] may be readily obtained by applying the Gibbs-Dalton rule in the form $p = \Sigma p_1$ using the equation (VII) to compute the p_1's. The equations for energy (53), entropy (54), and ψ (55), have already been given, and from these the equation for $\Sigma \nu_1 \mu_1$ may be formed and the equilibrium equation found, i.e.,

$$\left.\begin{aligned} \sum \nu_1 \mu_1 &\geqq 0, \\ \sum \nu_1 \log k_p = \sum \nu_1 \log p_0 x_1 &- \sum \frac{\nu_1 n_1 B_1}{v - B_1 n_1}, \end{aligned}\right\} \quad (129)\ [309]$$

where $\Sigma \nu_1 \log p_0 x_1$ is given by equation (114) [309]. The second term of the right hand member of (129) [309] may be written, using (VIIa) and omitting $\alpha_1, \alpha_2, \ldots$

$$-\frac{p}{Rt} \sum \nu_1 x_1 B_1 = \frac{p}{Rt}\left[\sum \nu_1 x_1 \frac{A_1}{Rt} - \sum \nu_1 x_1 \beta_1\right]. \quad (130)$$

Substituting in (129) [309] there is obtained

$$\sum \nu_1 \log p x_1 - \sum \nu_1 \log p_0 x_1 = \left[\frac{\Sigma \nu_1 x_1 A_1}{(Rt)^2} - \frac{\Sigma \nu_1 x_1 \beta_1}{Rt}\right] p. \quad (131)$$

Thus it is seen that at constant temperature the left hand member, or the quantity $\log K_p/K_0$ should vary with the pressure. For the reaction $N_2O_4 \rightarrow 2NO_2$ we may write

$$\log K_p/K_0 = -\left[\frac{(2\beta_1 + \beta_2)}{Rt} - \frac{(2A_1 + A_2)}{(Rt)^2}\right] x_1 p$$
$$+ \left[\frac{\beta_2}{Rt} - \frac{A_2}{(Rt)^2}\right] p, \quad (132)$$

where β_1, β_2, A_1, A_2, are the constants of the equation of state for the gases NO_2 (mol fraction x_1) and N_2O_4 (mol fraction x_2). At constant temperature and low pressure, x_1 the mol fraction of the simple species is small, and $\log K_p/K_0$ depends more largely on the second term of the right hand member, which is independent of x_1 but proportional to pressure. The coefficient of p, it should be noted, can be positive, negative or zero depending on the temperature, and of course the coefficient of x_1p has the same property although the temperature at which each coefficient vanishes will not in general be the same.

Certain considerations may be shown to make plausible the assumption that $2\beta_1 = \beta_2$, $2A_1 = A_2$; where β_1, A_1, β_2, A_2, are the constants in mols of the equations of state. Under such an assumption the last equation reduces to

$$\begin{aligned} \log K_p/K_0 &= \left[\frac{\beta_2}{Rt} - \frac{A_2}{(Rt)^2}\right](x_2 - x_1)\, p \\ &= \left[\frac{\beta_2}{Rt} - \frac{A_2}{(Rt)^2}\right]\left[\frac{1 - 3\alpha}{1 + \alpha}\right] p, \end{aligned} \tag{133}$$

where α is the fraction of N_2O_4 dissociated.

A recent paper by Verhoek and Daniels[61] contains material which affords a test of the formulation above. The measurements show that the values of $\log K_p/K_0$ do actually vary linearly with pressure over a range of pressure which however does not exceed one atm. The data have been used to prepare Fig. 2 illustrating the course of the experiments at three temperatures. The slopes of the lines do not appear to be in regular order as would be expected from the equation above. However, if the equation above were capable of representing the data, a line would start from the origin for every isothermal series of experiments forming a "fan" composed of lines in both the positive or upper part of the diagram and the lower or negative part. Eventually K_p will equal K_0 independent of the pressure but, as P increases, the sign of the right hand member would come to depend upon $(x_2 - x_1)$. A continuation of the exact investigation of this reaction evidently holds much of interest. The reformulations of the data[62, 63] on this reaction, using the ideal gas laws, which have appeared since the publication of Gibbs' papers, can add nothing to the thermodynamic theory as applied to cases of convertible components.

29. General Conclusions and the Equation of State of an Ideal Gas Mixture Having Convertible Components. The heat capacity at constant volume for a real gas possessing a coefficient $(\partial p/\partial t)_v$

which is constant and independent of temperature is the same as it would be for the gas in the ideal state at infinitely low pressure. This may be proved by considering the two general equations

$$\left(\frac{\partial \eta}{\partial v}\right)_t = \left(\frac{\partial p}{\partial t}\right)_v, \qquad [337]$$

and

$$\left(\frac{\partial \eta}{\partial t}\right)_v = \left(\frac{c_v}{t}\right).$$

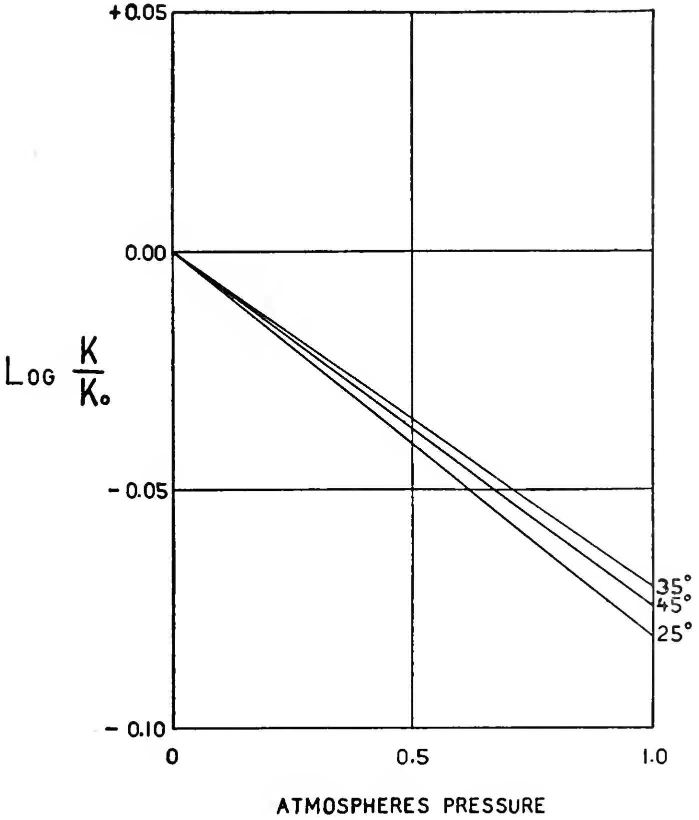

Fig. 2

Performing the operations indicated in [338] the following equation is deduced:

$$\left(\frac{\partial c_v}{\partial v}\right)_t = t\left(\frac{\partial^2 p}{\partial t^2}\right)_v. \tag{135}$$

Accordingly the right hand member of the latter vanishes for a substance whose $(\partial p/\partial t)_v$ coefficient is constant, and the conclusion follows that c_v is a function of temperature only. But no restriction has been put upon whether $(\partial p/\partial t)_v$ is to be taken at high pressures or low, for perfect or imperfect gases, and therefore c_v is the same whether the fluid is of great density or of vanishing density. A fluid following van der Waals' equation would possess the latter quality. Comparison of the heat capacity c_v of ether, for example, in the liquid phase and the gaseous phase will show that the heat capacities are equal for the substance in the two phases. This, however, is not to be taken as an indication that ether follows van der Waals' equation. As a matter of fact, however, $(\partial p/\partial t)_v$ is remarkably independent of temperature in the case of many substances, (in both the gaseous and liquid phases)[64] particularly non-polar substances in the dielectric constant sense of the term.

Assuming the gases NO_2 and N_2O_4 to be ideal the equation of state may be written $pv = Rt\,(n_1 + n_2)$ where n_1 and n_2 denote the number of mols of the two gases. Assume that one mol of N_2O_4 is dissociated to the extent α, the fraction dissociated. The quantity n_1 will be then given by 2α and n_2 by $(1 - \alpha)$ whence $pv = Rt(1 + \alpha)$. On the other hand [333] in terms of α becomes

$$\log p\,\frac{\alpha^2}{1 - \alpha^2} = A_0 + B_0 \log t - \frac{C_0}{t}$$

or

$$\frac{\alpha^2}{1 - \alpha^2} = A_0{}'\, t^{B_0}\, e^{-\frac{C_0}{t}}\,\frac{1}{p}, \tag{136}$$

where A_0, B_0 and C_0 are constants related to similar ones appearing in [333]. By means of the latter an expression for p

as a function of α and t is found and, using the equation for pv, another equation giving v in terms of α and t. These are

$$p = \frac{1 - \alpha^2}{\alpha^2} A_0' t^{B_0} e^{-\frac{C_0}{t}}, \tag{137}$$

$$v = \frac{\alpha^2}{1 - \alpha} A_0'' t^{1 - B_0} e^{\frac{C_0}{t}}, \tag{138}$$

where A_0'' is $\frac{R}{A_0'}$. From the equations it is clear that $(\partial p/\partial t)_v$ cannot be independent of temperature except in the strict limit of $p = 0$ or $t = \infty$, for

$$\left(\frac{\partial p}{\partial t}\right)_v = \frac{R}{v}(1 + \alpha) + \frac{Rt}{v}\left(\frac{\partial \alpha}{\partial t}\right)_v.$$

Equation [342] is the Gibbs-Dalton rule, $p = \Sigma p_1$, applied to the case of binary mixtures assuming equilibrium to subsist at all times. It is equivalent to the equation $p = \frac{Rt}{v}(1 + \alpha)$ where mols are used instead of masses. The equation for v above corresponds to [345]. Since the entropy and energy conform to the summation rules, [282], [283] may be easily formed in terms of mols from the foregoing, while the calculation of the specific heat capacity of the equilibrium mixture may be carried out by differentiating the energy equation [346] of Gibbs with respect to temperature at constant volume.

VI. On the Vapor-densities of Peroxide of Nitrogen, Formic Acid, Acetic Acid, and Perchloride of Phosphorus

(Gibbs, I, 372–403)

This section comprises material examined with a view to demonstrating the applicability of [309] or (114) [309]. Since 1879 a quantity of new density data for these substances has appeared, but no new facts or inferences can be gleaned by repeating Gibbs' treatment. In the case of the $N_2O_4 \rightarrow 2NO_2$ reaction Verhoek and Daniels' work, already referred to, has shown that the perfect gas laws are not sufficiently valid to warrant attempting a refined correlation on the usual basis. There is no doubt whatever that the same statement will hold true for the other gases or vapors listed in the heading of the section.

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K

THE THERMODYNAMICS OF STRAINED ELASTIC SOLIDS

THE CONDITIONS OF INTERNAL AND EXTERNAL EQUILIBRIUM FOR SOLIDS IN CONTACT WITH FLUIDS WITH REGARD TO ALL POSSIBLE STATES OF STRAIN OF THE SOLIDS

[*Gibbs, I, pp. 184–218*]

JAMES RICE

Note. In order to follow this part of Gibbs' work the reader must know something about the mathematical treatment of the relations which exist between the stresses set up in an elastic medium by the action of external forces on it, and the strains which accompany these stresses. In the study of the thermodynamics of these media, such relations take the place of the equation of state in the thermodynamics of a fluid medium. The treatment of Gibbs is formally somewhat more complicated than that usually employed, by reason of his desire at the outset to make use of two sets of axes of reference which need not be regarded as identical, although they are similar, i.e., capable of superposition (p. 185). It will therefore be advisable to deal with these matters in a less complicated manner at first. In consequence we shall have to prefix to the commentary proper a rather long exposition of the analysis of strain and stress, with some account of the thermodynamics of a single strained body.

I. Exposition of Elastic Solid Theory So Far As Needed for Following Gibbs' Treatment of the Contact of Fluids and Solids

1. Analysis of Strain. When a body is deformed or strained, its parts undergo a change of relative position. In order to deal with this in the classical mathematical way, we conceive the body to be constituted of particles each of which has in any assigned state of strain definite coordinates with regard to assigned axes of reference; and yet we compromise with these notions of molecular structure and also conceive that the material of the body is "smoothed out" to become a continuous medium. We picture a "physically small" element of the body around a particle, i.e., an element of volume small enough to be beyond our powers of handling experimentally and yet large enough to contain a very great number of molecules; the quotient of the mass of the molecules contained within this element by its volume being regarded as the density at the point.

If a body is strained, obviously some of its particles must be displaced from the position previously occupied in the system of reference. Yet displacement may not produce strain. Clearly there is no strain if each particle receives a displacement equal in magnitude and direction to that to which all the other particles are subject. Again a simple rotation, or a motion compounded of a simple translation and a simple rotation, will produce no strain. In short, strain involves not only displacement but also a difference of displacement for neighboring particles (which is not compatible with a simple rotation), and the business of the mathematician is to determine the most convenient mathematical way of stating how this *difference of displacement* varies for two neighboring particles P and Q supposing that one of them, P, is kept in mind all the time while the other one, Q, is conceived to be in turn any one of the other particles in an element of volume around P. If this statement when formulated turns out to be quantitatively the same for all the elements of volume, we call the strain "homogeneous;" otherwise it is "heterogeneous."

We will consider (with Gibbs) that the body is first in a "completely determined state of strain," which we shall call the "*state of reference.*" Let P' be the position of a point or particle of the body in this state. It is then strained from this state, and we denote by P the position of the same *particle.* Consider another particle, near to the former, whose position in the state of reference is Q' and after the strain is Q. The mathematical formulation of the nature of this strain will summarize all the essential information concerning the elongation of the element of length $P'Q'$ and also its change of orientation when it is displaced to PQ, and this for all possible positions of Q' in the neighborhood of P'; and this again, if the strain is heterogeneous, for all possible positions of P' in the body.

The use of the words "homogeneous" and "heterogeneous" in connection with strain must not lead to confusion with their use as referring to substances. A homogeneous material may very readily be subjected to a heterogeneous strain, as will appear presently. It is as well also at this point to realize what is meant by an elastically isotropic material as distinct from one which is elastically anisotropic (or aeolotropic). Thus we suppose that the body is deformed from its state of reference by a completely defined set of external forces acting on each element of volume (gravitational, for example; or definite mechanical pulls applied to definite elements of volume in the periphery of the body). Each element of length $P'Q'$ in the body is subject to a definite change in length and direction. Suppose now that all the external forces remain unchanged in magnitude but all are changed by the same amount in direction, then the strain in the linear element $P'Q'$, i.e., its change in magnitude and direction from the state of reference, will not in general remain as before; but if the body is isotropic a linear element $P'R'$ which bears the same relation of direction to the directionally changed forces as did $P'Q'$ to the external forces formerly, will experience the same strain as that to which $P'Q'$ was subject in the first case. But for an anisotropic (crystalline) body even this statement is not in general true. These definitions in general terms will be more clearly stated in precise mathematical form presently; but the fact mentioned embodies the essence of the distinction between anisotropy and isotropy.

Before proceeding to a general mathematical treatment of strain it may be advisable to consider one or two special cases where there are certain simplifying conditions. Imagine for example that all points are displaced in one direction, parallel to the axis OX' say, and that the displacement of the point $P'(x', y', z')$ is a function of x' only. Representing this displacement by $u(x')$ (or briefly by u), we have

$$x = x' + u(x'), \qquad y = y', \qquad z = z',$$

where the coordinates of the point P after the strain are x, y, z. Let Q' be a point adjacent to P' whose coordinates in the state of reference are $x' + \xi'$, y', z'; the coordinates of Q, i.e., the position after the strain, are

$$x' + \xi' + u(x' + \xi'), \qquad y, \qquad z,$$

where $u(x' + \xi')$ is the same function of the argument $x' + \xi'$ that $u(x')$ is of x'. Hence the linear element $P'Q'$ has been altered from a length ξ' to a length $\xi' + u(x' + \xi') - u(x')$, besides of course experiencing a bodily translation which is of no importance in discussing the strain. Thus the alteration in length of the linear element is

$$u(x' + \xi') - u(x'),$$

which by Taylor's theorem is equal to

$$\frac{du}{dx'}\xi' + \tfrac{1}{2}\frac{d^2u}{dx'^2}\xi'^2 + \dots .$$

If the differential coefficient du/dx' does not vary in value appreciably over a range within which we choose the value of ξ', we may neglect the terms in ξ'^2 etc. (Thus if $P'Q'$ is a range of length extending over a few molecules in the actual body this proviso is the same as that referred to by Gibbs on page 185, line 20.) Under these circumstances the length of $P'Q'$, viz., ξ', is altered to $\xi'(1 + du/dx')$, and hence du/dx' is the fraction of elongation of the body at P', viz., the ratio of the change in length to the original length. Gibbs in his discussion actually uses the differential coefficient dx/dx', but it is readily seen that this is just $1 + du/dx'$, i.e., the ratio of elongation, or the "variation" of the length in the strict meaning of "variation," viz., the ratio of the varied value of a quantity to its previous value. If $u(x')$ is a linear function of x' so that du/dx' is constant over the whole body, the elongation has the same value everywhere, and the strain is homogeneous. Otherwise du/dx' varies from element to element of the body, and is in fact a function of x' itself, so that the value of du/dx' depends on where the point P' of the element is situated in the body, and the strain is "heterogeneous." Nevertheless, on account of the proviso mentioned above, we can regard the strain as being homogeneous throughout any assigned physically small element of volume. If the length actually contracts, the extension du/dx' is negative.

As another simple example consider again the case in which all particles are displaced parallel to OX', but now taking the displacement to be a function of y', the distance of the particle from a plane parallel to which the displacement takes place. Now choose Q', the neighbor of P', to be a point such that $P'Q'$ is perpendicular to the direction of the displacements.

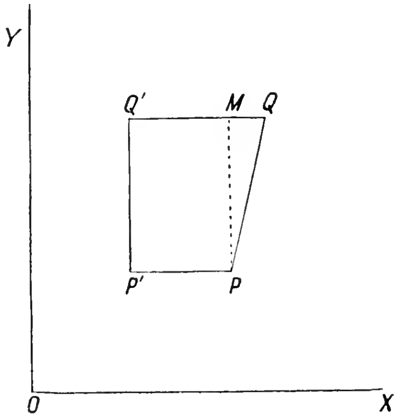

FIG. 1

Thus if x', y', z' are the coordinates of P' and x, y, z are the coordinates of its displaced position P,

$$x = x' + u(y'), \qquad y = y', \qquad z = z'.$$

Also if x', $y' + \eta'$, z' are the coordinates of the undisplaced position Q' of the "neighbor," its displaced coordinates are

$$x' + u(y' + \eta'), \qquad y' + \eta', \qquad z'.$$

The displacement $P'P$ is $u(y')$ and the displacement $Q'Q$ is $u(y' + \eta')$ or $u(y') + (du/dy')\eta'$. Hence MQ in Fig. 1 is

$(du/dy')\eta'$ and the angle QPM has for its trigonometrical tangent the value du/dy'. The figure shows that this strain is what is called a "shear." A bar shaped element of volume which is extended parallel to the axis OZ' (perpendicular to the plane of the paper) and whose section by the plane $OX'Y'$ is $P'Q'R'S'$ (Fig. 2), is displaced to a position whose section is $PQRS$. This is equivalent to a simple displacement of the bar as a whole from $P'Q'R'S'$ to $PMNS$ and a real strain or change of shape from $PMNS$ to $PQRS$. This latter is the "shear" and its magnitude is measured by the tangent of the angle QPM (or simply by the angle itself when the strain is so small that the tangent of the angle and its radian measure are practically identical), i.e., by du/dy'. If u is a linear function of y', the shear is homogeneous throughout the body; otherwise it is heterogeneous and the amount of shearing varies from point to point of the body.

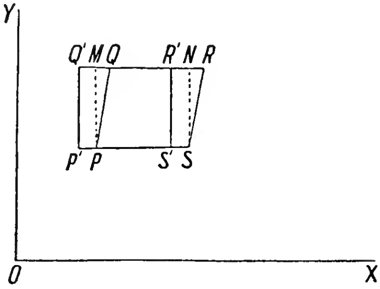

FIG. 2

When we undertake a general analysis of strain these special cases give us a hint how to proceed. The point P' whose coordinates are x', y', z' experiences a displacement whose components we represent by $u(x', y', z')$, $v(x', y', z')$, $w(x', y', z')$, for the displacement must have some functional relationship with the position of P' if analysis is to be possible at all.*

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* Will the reader please note that we are, for the time being, referring the body before *and after* the strain to the same axes OX', OY', OZ'. Formally Gibbs' procedure is a little wider since he refers the body after

Hence the coordinates of the point in its displaced position, viz., P'', are given by

$$x'' = x' + u(x', y', z'), \qquad y'' = y' + v(x', y', z'),$$
$$z'' = z' + w(x', y', z'). \tag{1}$$

Consider a neighboring point whose undisplaced position is Q' with the coordinates

$$x' + \xi', y' + \eta', z' + \zeta'.$$

After the displacement, the coordinates (of Q'') are

$$x' + \xi' + u(x' + \xi', y' + \eta', z' + \zeta'),$$

and two similar expressions. Neglecting as before and for the same reason the differential coefficients higher than the first, these become $x'' + \xi''$, $y'' + \eta''$, $z'' + \zeta''$, where

$$\left.\begin{aligned}
\xi'' &= \xi' + \frac{\partial u}{\partial x'}\xi' + \frac{\partial u}{\partial y'}\eta' + \frac{\partial u}{\partial z'}\zeta',\\
\eta'' &= \eta' + \frac{\partial v}{\partial x'}\xi' + \frac{\partial v}{\partial y'}\eta' + \frac{\partial v}{\partial z'}\zeta',\\
\zeta'' &= \zeta' + \frac{\partial w}{\partial x'}\xi' + \frac{\partial w}{\partial y'}\eta' + \frac{\partial w}{\partial z'}\zeta'.
\end{aligned}\right\} \tag{2}$$

(For convenience and brevity we drop the bracketed coordinates after the symbols u, v, w; but it must not be forgotten that u is to be understood as the function $u(x', y', z')$, etc).

It will be convenient to introduce single letter symbols to

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the strain to a different set of axes OX, OY, OZ. The two sets of axes are not necessarily identical, but he regards them as "similar, i.e., capable of superposition"; so that if one set is orthogonal, then also is the other. At the outset, however, there is an element of simplification in keeping the same set of axes; but in order that there may be no confusion later when we adopt Gibbs' wider analysis we are now referring to the coordinates of the displaced point as x'', y'', z'' instead of x, y, z, thus keeping the latter triad of letters to represent, as Gibbs does, the coordinates of the displaced point with reference to a second system of axes.

replace the differential coefficients, so we shall write these equations as

$$\left.\begin{aligned}\xi'' &= e_{11}\xi' + e_{12}\eta' + e_{13}\zeta',\\ \eta'' &= e_{21}\xi' + e_{22}\eta' + e_{23}\zeta',\\ \zeta'' &= e_{31}\xi' + e_{32}\eta' + e_{33}\zeta',\end{aligned}\right\} \tag{3}$$

where*

$$\left.\begin{aligned}
e_{11} &= 1 + \frac{\partial u}{\partial x'} = \frac{\partial x''}{\partial x'}, & e_{12} &= \frac{\partial u}{\partial y'} = \frac{\partial x''}{\partial y'}, & e_{13} &= \frac{\partial u}{\partial z'} = \frac{\partial x''}{\partial z'},\\
e_{21} &= \frac{\partial v}{\partial x'} = \frac{\partial y''}{\partial x'}, & e_{22} &= 1 + \frac{\partial v}{\partial y'} = \frac{\partial y''}{\partial y'}, & e_{23} &= \frac{\partial v}{\partial z'} = \frac{\partial y''}{\partial z'},\\
e_{31} &= \frac{\partial w}{\partial x'} = \frac{\partial z''}{\partial x'}, & e_{32} &= \frac{\partial w}{\partial y'} = \frac{\partial z''}{\partial y'}, & e_{33} &= 1 + \frac{\partial w}{\partial z'} = \frac{\partial z''}{\partial z'}.
\end{aligned}\right\} \tag{4}$$

2. Homogeneous Strain. In order to grasp most readily the physical interpretation of these "strain coefficients" which are denoted by the symbols e_{rs}, let us consider the case in which u, v, w (and therefore x'', y'', z'') are *linear* functions of x', y', z'. Under such a limitation, the quantities e_{rs} are uniform in value throughout the body; in other words the strain is homogeneous.

Now it is very important to remember at this juncture that it is not so much the actual displacements of the various points which determine the strain, as the *differences* between the displacements of the various points. In Fig. 3 P' is displaced to P'' and Q' to Q''; but to obtain a clear idea of the strain in the part of the body surrounding P', we must imagine the whole body translated *without change of shape and without rotation*, i.e., as a rigid body, so as to bring the point P'' back to its former position P'. This will bring the point Q'' to R'', where $Q''R''$ is parallel and equal to $P''P'$. The magnitude and direction of the line $Q'R''$ is the vector which, when estimated for all Q' points in the neighborhood of P', would give us the necessary information for calculating the strain. Now the components of the vector length $Q'R''$, the "differential displacement" of Q' with reference to P', are $\xi'' - \xi'$, $\eta'' - \eta'$, $\zeta'' - \zeta'$ and are therefore equal to the expressions

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* We are of course using the well-known notation of the "curly" ∂ for partial differentiation. When Gibbs wrote his paper this device for indicating a partial differential coefficient had not established itself universally, and many writers used the ordinary italic *d* to indicate total and partial differential alike, relying on the reader's own knowledge to make the necessary distinction in each situation. But as, of course, the differential coefficients in [354] and in subsequent equations are partial, we venture to make this small change in Gibbs' notation in view of the universal practice adopted in these matters nowadays.

$$\left.\begin{aligned}(e_{11} - 1)\xi' + e_{12}\eta' + e_{13}\zeta',\\ e_{21}\xi' + (e_{22} - 1)\eta' + e_{23}\zeta',\\ e_{31}\xi' + e_{32}\eta' + (e_{33} - 1)\zeta',\end{aligned}\right\} \tag{5}$$

which are linear functions of ξ', η', ζ' if e_{11}, e_{12}, e_{13}, . . . e_{33} are constants.

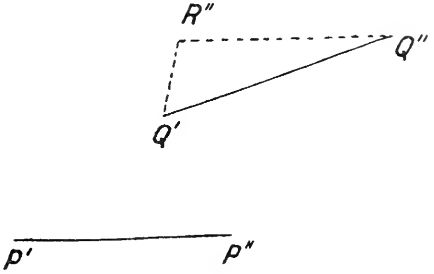

FIG. 3

Let us impose for a moment a simplifying condition with regard to these nine strain constants and assume that $e_{12} = e_{21}$, $e_{23} = e_{32}$, $e_{31} = e_{13}$. It will be very convenient for a moment to write a for $e_{11} - 1$, b for $e_{22} - 1$, c for $e_{33} - 1$, f for e_{23} or e_{32}, g for e_{31} or e_{13}, h for e_{12} or e_{21}. Thus

$$\left.\begin{aligned}\xi'' - \xi' &= a\xi' + h\eta' + g\zeta',\\ \eta'' - \eta' &= h\xi' + b\eta' + f\zeta',\\ \zeta'' - \zeta' &= g\xi' + f\eta' + c\zeta'.\end{aligned}\right\} \tag{6}$$

Taking P' as a local origin, and axes of reference through P' parallel to OX', OY', OZ' ("local axes" at P'), let us suppose the family of similar and similarly placed quadric surfaces constructed, which are represented, in the "local" coordinates ξ', η', ζ', by the equation

$$a\xi'^2 + b\eta'^2 + c\zeta'^2 + 2f\eta'\zeta' + 2g\zeta'\xi' + 2h\xi'\eta' = k,$$

where k is a constant which has a definite value for each member of the family. One member of this family will pass through Q' and, if we recall the statements made concerning quadric surfaces in the author's Mathematical Note (this volume, Article B, p. 15), it will be seen by reference to (6) that the differential displacement $Q'R''$ of the point Q' is normal to this surface at this point. The result of this will be that points originally on a straight line will still lie on a straight line after the strain. (The expressions in (6) are *linear* in ξ', η', ζ'.) But in general the angle between two lines will be altered in value; in particular two lines at right angles to each other before the strain will not be at right angles after it. However, there is an exception to this general statement. There are three mutually orthogonal directions and any lines which are parallel to these before the strain remain at right angles to each other after the strain. These directions are in fact the directions of the three principal axes of the quadric surface; for if Q' is on one of these, then, since $Q'R''$ is normal to the surface at Q', R'' is on the axis too, and the lines $P'Q'$ and $P'R''$ are coincident. But by construction $P''Q''$ is parallel to $P'R''$; therefore it is parallel to $P'Q'$. Hence the three principal axes are displaced into three lines parallel to them respectively, and so are at right angles to each other as before.

To prove this we apparently had to restrict our reasoning by assuming that $e_{23} = e_{32}$, etc. We can remove this restriction however and still arrive at the same result. To show this we must resort to a simple artifice. Take the first expression in (5), and treat it thus:

$$(e_{11} - 1)\,\xi' + e_{12}\eta' + e_{13}\zeta' = (e_{11} - 1)\,\xi' + \frac{e_{12} + e_{21}}{2}\,\eta'$$

$$+ \frac{e_{31} + e_{13}}{2}\,\zeta' + \frac{e_{12} - e_{21}}{2}\,\eta' - \frac{e_{31} - e_{13}}{2}\,\zeta'.$$

Treat the remaining two in a similar fashion and for temporary convenience put

$$a \text{ for } e_{11} - 1, \quad f \text{ for } \frac{e_{23} + e_{32}}{2}, \quad p \text{ for } \frac{e_{23} - e_{32}}{2},$$

$$b \text{ for } e_{22} - 1, \quad g \text{ for } \frac{e_{31} + e_{13}}{2}, \quad q \text{ for } \frac{e_{31} - e_{13}}{2},$$

$$c \text{ for } e_{33} - 1, \quad h \text{ for } \frac{e_{12} + e_{21}}{2}, \quad r \text{ for } \frac{e_{12} - e_{21}}{2}.$$

We then have

$$\left.\begin{aligned} \xi'' - \xi' &= a\xi' + h\eta' + g\zeta' + r\eta' - q\zeta', \\ \eta'' - \eta' &= h\xi' + b\eta' + f\zeta' + p\zeta' - r\xi', \\ \zeta'' - \zeta' &= g\xi' + f\eta' + c\zeta' + q\xi' - p\eta'. \end{aligned}\right\} \qquad (7)$$

If we take the first three terms on the right hand side of each equation in (7), it is clear that they represent, as before, a differential displacement which at each point is normal to the corresponding member of a family of similar quadric surfaces. As we have seen, this part of the whole differential displacement still leaves three certain lines orthogonal and unaffected in direction. Now consider the last two terms. They represent a displacement due to a small rotation about a line whose direction cosines are proportional to p, q, r. This is readily seen by observing that

$$p(r\eta' - q\zeta') + q(p\zeta' - r\xi') + r(q\xi' - p\eta') = 0$$

and

$$\xi'(r\eta' - q\zeta') + \eta'(p\zeta' - r\xi') + \zeta'(q\xi' - p\eta') = 0;$$

thus the small displacement of which the components are $r\eta' - q\zeta'$, $p\zeta' - r\xi'$, $q\xi' - p\eta'$, is at right angles not only to the line whose direction cosines are proportional to p, q, r, but also to the line $P'Q'$, whose direction cosines are of course proportional to ξ', η', ζ'. But a rotation does not disturb the angles between two lines. Hence the result follows as before, so that there are in every case of a small strain three particular lines, the so called "principal axes of strain," which are not only mutually orthogonal before the strain, but remain so after it, although in general they are not pointing in the same directions after as before. This is a result used by Gibbs and demonstrated by him in a different manner (Gibbs, I, 205 *et seq*). On page 204 also occurs the sentence: "We have already had occasion to remark that the state of strain of an element considered without reference to directions in space is capable of only six independent variations." This remark is illustrated by the result which we have just obtained, since although there are *nine* strain-coefficients, the strain, apart from the rotation which produces no relative displacement of neighboring parts, depends on the *six* quantities

$$e_{11}, \qquad e_{22}, \qquad e_{33}, \qquad \frac{e_{23}+e_{32}}{2}, \qquad \frac{e_{31}+e_{13}}{2}, \qquad \frac{e_{12}+e_{21}}{2}.$$

Gibbs then continues: "Hence it must be possible to express the state of strain of an element by six functions of $\partial x/\partial x'$, ... $\partial z/\partial z'$, which are independent of the position of the element." The functions chosen by Gibbs are not so formally simple as those written above and have a certain appearance of arbitrariness about them. So we will address ourselves to the task of explaining how the six functions defined in [418] and [419] naturally arise in a further discussion of strain. Indeed, the whole of the material treated in Gibbs, I, 205–211 may prove troublesome to follow without some help over analytical difficulties, which will now be given. The treatment which follows will present the matter from a somewhat different angle and at the same time bring out the physical nature of the e_{rs} coefficients.

Let us revert to equations (3) and use them to determine the length of $P''Q''$ as a function of the local coordinates of Q', the original position of Q'', with reference to the axes through P', the original position of P''. It is easy to see that

$$\begin{aligned}\overline{P''Q''}^2 &= \xi''^2 + \eta''^2 + \zeta''^2 \\ &= e_1\xi'^2 + e_2\eta'^2 + e_3\zeta'^2 + 2e_4\eta'\zeta' + 2e_5\zeta'\xi' + 2e_6\xi'\eta', \qquad (8)\end{aligned}$$

where

$$\left.\begin{aligned} e_1 &= e_{11}^2 + e_{21}^2 + e_{31}^2, \\ e_2 &= e_{12}^2 + e_{22}^2 + e_{32}^2, \\ e_3 &= e_{13}^2 + e_{23}^2 + e_{33}^2, \\ e_4 &= e_{12}e_{13} + e_{22}e_{23} + e_{32}e_{33}, \\ e_5 &= e_{13}e_{11} + e_{23}e_{21} + e_{33}e_{31}, \\ e_6 &= e_{11}e_{12} + e_{21}e_{22} + e_{31}e_{32}. \end{aligned}\right\} \qquad (9)$$

Choose for the moment a special case, letting the point Q' be placed on the local axis of x' at P', so that its local coordinates are ξ', 0, 0. It follows from (8) that

$$\overline{P''Q''}^2 = e_1\xi'^2 = e_1\overline{P'Q'}^2.$$

Thus $(e_1)^{\frac{1}{2}}$ is the "ratio of elongation" parallel to OX', and $(e_2)^{\frac{1}{2}}$ and $(e_3)^{\frac{1}{2}}$ can be interpreted in a similar manner. It was mentioned above that two lines at right angles to each other before the strain will not remain so after it. We shall show how this fact is connected with the e_4, e_5, e_6 quantities. For let us consider Q' to be a point in the local plane of x' y' at P', its local coordinates being ξ', η', 0. Drop perpendiculars $Q'M'$, $Q'N'$ on the local axes of x' and y' at P'. Let Q'', M'', N'' be the positions of these points after the strain. From the result obtained just above

$$\begin{aligned} \overline{P''M''}^2 &= e_1\overline{P'M'}^2, \\ \overline{P''N''}^2 &= e_2\overline{P'N'}^2. \end{aligned}$$

From (8) we obtain

$$\overline{P''Q''}^2 = e_1\xi'^2 + e_2\eta'^2 + 2e_6\xi'\eta',$$

and so

$$\overline{P''Q''}^2 = \overline{P''M''}^2 + \overline{P''N''}^2 + 2\frac{e_6}{(e_1e_2)^{\frac{1}{2}}}\cdot P''M''\cdot P''N''.$$

But by the application of elementary trigonometry to the parallelogram $P''M''Q''N''$

$$\overline{P''Q''}^2 = \overline{P''M''}^2 + \overline{P''N''}^2 + 2P''M''\cdot P''N''\cdot\cos(N''P''M'').$$

Hence

$$\cos (N''P''M'') = \frac{e_6}{(e_1 e_2)^{\frac{1}{2}}}, \tag{10}$$

and similar results can be obtained for the other pairs of axes. A glance at Fig. 4 shows that the rectangle $P'M'Q'N'$ has suffered a shear to the shape $P''M''Q''N''$. (It is in general also subject to a rotation.) The shear is measured by the angle $L''P''N''$ whose sine is by equation (10) equal to $e_6/(e_1e_2)^{\frac{1}{2}}$. If the strains are sufficiently small we can simplify this. Recalling the original definitions of the e_{rs} coefficients in (4), we see that

$$e_{11} - 1,\ e_{22} - 1,\ e_{33} - 1,\ e_{23},\ e_{32},\ e_{31},\ e_{13}.\ e_{12},\ e_{21}$$

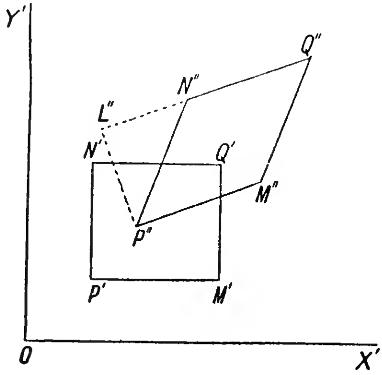

FIG. 4

are small compared to unity if the *relative* displacement of two points is a small fraction of their distance apart. Hence, by (9), e_1, e_2, e_3 each differ from unity by a small amount. Also in the definition of e_6 the third term is the product of two small quantities, the second term differs from e_{21} by a small fraction of e_{21}, and the first term differs from e_{12} by a small fraction of e_{12}. Thus, apart from a negligible error, the sine of $L''P''N''$ is equal to $e_{12} + e_{21}$. The angle being also small in this case, its value, that is the shear of the lines originally parallel to OX' and OY', is practically $e_{12} + e_{21}$; this in fact measures very closely the amount by which the angle between these lines has changed from a right angle. The shears of lines parallel originally to the axes OY' and OZ', and of those parallel to the axes OZ' and OX', are likewise given to a close approximation by e_4 and e_5, respectively, or practically $e_{23} + e_{32}$ and $e_{31} + e_{13}$.

Now we know that there is one set of axes of reference, for which there is no shear. Suppose we had chosen them at the outset and carried through the analysis just finished, then three of six strain functions calculated as in (9) would be zero, viz. the three indicated by the suffixes 4, 5, 6. To make this as definite as possible let us indicate these three principal axes of strain by OL', OM', ON', and let the coordinates of Q', relative to three local axes through P' parallel to these, be denoted by the letters λ', μ', ν'. We should arrive at a result similar to (8) viz.,

$$\overline{P''Q''}^2 = \epsilon_1\lambda'^2 + \epsilon_2\mu'^2 + \epsilon_3\nu'^2 + 2\epsilon_4\mu'\nu' + 2\epsilon_5\nu'\lambda' + 2\epsilon_6\lambda'\mu',$$

where ϵ_1, ϵ_2, ϵ_3, etc., would be six strain functions such that $(\epsilon_1)^{\frac{1}{2}}$ would be the ratio of elongation parallel to OL', etc., and also such that the cosine of the angle between two lines originally parallel to OL' and OM' would be $\epsilon_6/(\epsilon_1\epsilon_2)^{\frac{1}{2}}$. But as this angle still remains a right angle, ϵ_6 would have to be zero and similarly for ϵ_4 and ϵ_5. Hence we would arrive at the result

$$\overline{P''Q''}^2 = \epsilon_1\lambda'^2 + \epsilon_2\mu'^2 + \epsilon_3\nu'^2.$$

In his discussion Gibbs indicates the three "principal ratios of elongation" by the letters r_1, r_2, r_3, so that his notation and ours are connected by

$$\epsilon_1 = r_1^2, \qquad \epsilon_2 = r_2^2, \qquad \epsilon_3 = r_3^2.$$

Certain relations, very necessary to our progress, between the ϵ_r and the e_r symbols can now be obtained very elegantly by an artifice depending on a theorem concerning quadric surfaces quoted in the Mathematical Note. Keeping P' as our local origin, allow Q' to move about on a locus of such a nature that the corresponding positions of Q'' lie on a sphere of radius b around P'' as centre. By (8) we see that the equation of this locus in the ξ', η', ζ' coordinates is

$$e_1\xi'^2 + e_2\eta'^2 + e_3\zeta'^2 + 2e_4\eta'\zeta' + 2e_5\zeta'\xi' + 2e_6\xi'\eta' = b^2.$$

It is an ellipsoid, and its position *in the body* is entirely independent of what axes of reference we choose. So the same surface referred to the principal axes as axes of coordinates has the equation

$$\epsilon_1\lambda'^2 + \epsilon_2\mu'^2 + \epsilon_3\nu'^2 = b^2.$$

By a theorem on quadric surfaces quoted in the Mathematical Note, observing that

$\xi', \eta' \zeta'$ correspond to x, y, z in the note,
λ', μ', ν' correspond to x', y', z' in the note,
$e_1, e_2, e_3, e_4, e_5, e_6$ correspond to a, b, c, f, g, h in the note,
$\epsilon_1, \epsilon_2, \epsilon_3$ correspond to a', b', c' in the note,

we arrive at these three results:

$$\left.\begin{aligned} e_1 + e_2 + e_3 &= \epsilon_1 + \epsilon_2 + \epsilon_3, \\ e_2e_3 + e_3e_1 + e_1e_2 - e_4^2 - e_5^2 - e_6^2 &= \epsilon_2\epsilon_3 + \epsilon_3\epsilon_1 + \epsilon_1\epsilon_2, \\ \begin{vmatrix} e_1 & e_6 & e_5 \\ e_6 & e_2 & e_4 \\ e_5 & e_4 & e_3 \end{vmatrix} &= \epsilon_1\epsilon_2\epsilon_3. \end{aligned}\right\} \tag{11}$$

Now let the reader look at the equations (9) which give e_1, e_2, etc., in terms of the squares and products of the e_{rs} coefficients, and refer to the well-known rule for multiplying determinants which will be found in any text of algebra. He will find that the determinant in (11) is the square of the determinant

$$\begin{vmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{vmatrix}. \tag{12}$$

Thus the last of the equations in (11), on extracting the square root, is equivalent to

$$\begin{vmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{vmatrix} = r_1r_2r_3, \tag{13}$$

which is essentially equation [442], the third equation of (11) being essentially the third equation of [439]. Our equations differ from those of Gibbs in the greater generality which he adopts concerning axes of reference before and after strain. But this restriction we shall be able to eliminate presently, with no great trouble. In the meantime let us continue with the other two equations in (11). A glance at (9) shows that the first is just

$$\begin{aligned} e_{11}^2 + e_{12}^2 + e_{13}^2 + e_{21}^2 + e_{22}^2 + e_{23}^2 + e_{31}^2 + e_{32}^2 + e_{33}^2 \\ = r_1^2 + r_2^2 + r_3^2. \end{aligned} \tag{14}$$

The second of (11) gives a little more trouble; but the reader may take it on faith, if he does not care to go through the straightforward algebraic operations, that the following result can be verified. If one squares the nine first minors of the determinant (12) and adds them then the sum is equal to

$$e_2e_3 + e_3e_1 + e_1e_2 - e_4^2 - e_5^2 - e_6^2.$$

(A less tedious method of showing this would have involved us rather too deeply in the theory of determinants.) Hence, by the second equation of (11),

$$\begin{aligned} E_{11}^2 + E_{22}^2 + E_{33}^2 + E_{21}^2 + E_{22}^2 + E_{23}^2 + E_{31}^2 + E_{32}^2 \\ + E_{33}^2 = r_2^2r_3^2 + r_3^2r_1^2 + r_1^2r_2^2, \end{aligned} \tag{15}$$

where we are representing the first minor of e_{11} in the determinant of the e_{rs} by E_{11}, that of e_{12} by E_{12}, and so on. (The use of this double suffix notation is obviously of great convenience at the moment. The E_{rs} used here must not be confused by the reader with the symbol E used by Gibbs without any suffix, to which we will be referring presently.) Equations (14) and (15) are essentially the first two of the equations [439].

If we consider a rectangular parallelopiped whose sides are parallel to the principal axes and each of unit length, we know that it remains a parallelopiped after the strain (although it may be rotated) and its sides become r_1, r_2, r_3, respectively. Hence $r_1r_2r_3$ is the ratio of enlargement of volume, and so we see that this is a physical interpretation of the determinant (12), while the determinant in (11) is of course equal to the square of that ratio. Further, the sum of the squares of the nine first minors of (12) is equal to the sum of the squares of the ratios of enlargement of three bounded plane surfaces, respectively parallel to the three principal planes of the strain. Of course the sum of the squares of the nine e_{rs} coefficients is equal to the sum of the squares of the three principal ratios of elongation.

The interpretation of these results in terms of ratios of enlargement is of some importance. Equation (13), which is really the third equation of (11), is an especially useful result and is involved in Gibbs' equation [464]. The first equation of (11) is perhaps the least important of the three for our purpose, but the second result in the form of equation (15) plays a part at one or two points of Gibbs' treatment, e.g., at equation [463] and still earlier on pages 192, 193. It will be well to pause a moment to consider the geometrical significance of the nine minor determinants E_{11}, E_{12}, etc. To this end let us imagine a triangle $P'Q_1'Q_2'$ in the unstrained state such that the local coordinates of Q_1', Q_2', with reference to the local axes at P', are ξ_1', η_1', ζ_1' and ξ_2', η_2', ζ_2'. After the strain the triangle will assume the position $P''Q_1''Q_2''$. If ξ_1'', η_1'', ζ_1'' and ξ_2'', η_2'', ζ_2'' are the coordinates of Q_1'' and Q_2'' with reference to local axes at P'' parallel to the original axes we have by (3) the following relations:

$$\left.\begin{aligned}\xi_1'' &= e_{11}\xi_1' + e_{12}\eta_1' + e_{13}\zeta_1', & \xi_2'' &= e_{11}\xi_2' + e_{12}\eta_2' + e_{13}\zeta_2',\\ \eta_1'' &= e_{21}\xi_1' + e_{22}\eta_1' + e_{23}\zeta_1', & \eta_2'' &= e_{21}\xi_2' + e_{22}\eta_2' + e_{23}\zeta_2',\\ \zeta_1'' &= e_{31}\xi_1' + e_{32}\eta_1' + e_{33}\zeta_1', & \zeta_2'' &= e_{31}\xi_2' + e_{32}\eta_2' + e_{33}\zeta_2'.\end{aligned}\right\} \quad (16)$$

Denote the area of the triangle $P'Q_1'Q_2'$ by K' and that of $P''Q_1''Q_2''$ by K''. The projection of the triangle $P'Q_1'Q_2'$ on the local plane of reference perpendicular to the axis of x' is a triangle whose corners have the η, ζ coordinates 0, 0; η_1', ζ_1'; η_2', ζ_2'. By a well known rule its area is $\frac{1}{2}(\eta_1'\zeta_2' - \eta_2'\zeta_1')$, and similar expressions hold for other projections. Now the area of a projection is equal to the product of the projected area and the cosine of the angle between the original plane and the plane of the projection, which is the angle between the normals to the planes. So if α', β', γ' are the direction cosines of the normal to the plane of $P'Q_1'Q_2'$, and α'', β'', γ'' those of the normal to the plane of $P''Q_1''Q_2''$, we have the following results:

$$\left.\begin{aligned} K'\alpha' &= \tfrac{1}{2}(\eta_1'\zeta_2' - \eta_2'\zeta_1'), & K''\alpha'' &= \tfrac{1}{2}(\eta_1''\zeta_2'' - \eta_2''\zeta_1''),\\ K'\beta' &= \tfrac{1}{2}(\zeta_1'\xi_2' - \zeta_2'\xi_1'), & K''\beta'' &= \tfrac{1}{2}(\zeta_1''\xi_2'' - \zeta_2''\xi_1''),\\ K'\gamma' &= \tfrac{1}{2}(\xi_1'\eta_2' - \xi_2'\eta_1'), & K''\gamma'' &= \tfrac{1}{2}(\xi_1''\eta_2'' - \xi_2''\eta_1'').\end{aligned}\right\} \quad (17)$$

If one now uses equations (16), and is careful to keep to the convention about the signs of the first minors as explained in the note, it is not very troublesome to prove that

$$\begin{aligned}\eta_1''\zeta_2'' - \eta_2''\zeta_1'' = E_{11}(\eta_1'\zeta_2' - \eta_2'\zeta_1') + E_{12}(\zeta_1'\xi_2' - \zeta_2'\xi_1')\\ + E_{13}(\xi_1'\eta_2' - \xi_2'\eta_1'),\end{aligned}$$

and two similar results which can be succinctly written

$$\left.\begin{aligned} K''\alpha'' &= K'(E_{11}\alpha' + E_{12}\beta' + E_{13}\gamma'),\\ K''\beta'' &= K'(E_{21}\alpha' + E_{22}\beta' + E_{23}\gamma'),\\ K''\gamma'' &= K'(E_{31}\alpha' + E_{32}\beta' + E_{33}\gamma').\end{aligned}\right\} \qquad (18)$$

These are essentially the steps by which one passes from equation [381] to equation [382], K' and K'' being the Ds' and Ds'' of Gibbs. (There is of course at the moment some restriction on our e_{rs} and E_{rs} symbols, i.e., our differential coefficients and the determinants constructed from them, due to our restriction as to the axes chosen in the strained system; we have already referred to this and it will be removed shortly; for the moment it involves us in the use of doubly accented symbols such as ξ'', K'', α'', etc., so as to avoid confusion later when we widen our choice of axes.)

The interpretation of the quantities E_{rs} as determining superficial enlargement caused by the strain is very clearly indicated in (18), and a very elegant analogy can be exhibited between equations (18) and the equations (3) in which the e_{rs} quantities obviously determine linear enlargement. To this end we remind ourselves that an *oriented* plane area is a vector quantity, and is therefore representable by a point such that the radius vector to it is proportional to the area and is parallel to the normal. Thus the triangle $P'Q_1'Q_2'$ can be represented in orientation and magnitude by a point whose coordinates are

X', Y', Z' where $X' = K'\alpha', Y' = K'\beta', Z' = K'\gamma'$. Similarly a point whose coordinates are X'', Y'', Z'', where $X'' = K''\alpha''$, etc., can represent the triangle $P''Q_1''Q_2''$. The equations (18) can then be written

$$\left.\begin{aligned} X'' &= E_{11}X' + E_{12}Y' + E_{13}Z', \\ Y'' &= E_{21}X' + E_{22}Y' + E_{23}Z', \\ Z'' &= E_{31}X' + E_{32}Y' + E_{33}Z'. \end{aligned}\right\} \tag{19}$$

The reader will probably feel intuitively that, as can be established by definite proof, by choosing the principal axes of strain as the axes of reference, we can reduce the nine coefficients to a form in which $E_{23} + E_{32}$, $E_{31} + E_{13}$, $E_{12} + E_{21}$ are zero, and E_{11}, E_{22}, E_{33} become the *principal* ratios of superficial enlargement, i.e., r_2r_3, r_3r_1, r_1r_2. Squaring and adding the equalities in (19) we obtain

$$K''^2 = E_1X'^2 + E_2Y'^2 + E_3Z'^2 + 2E_4Y'Z' + 2E_5Z'X' + 2E_6X'Y',$$

where

$$\left.\begin{aligned} E_1 &= E_{11}^2 + E_{21}^2 + E_{31}^2 \\ &\text{and two similar equations,} \\ E_4 &= E_{12}E_{13} + E_{22}E_{23} + E_{32}E_{33} \\ &\text{and two similar equations.} \end{aligned}\right\} \tag{20}$$

An application of the theorem in the Mathematical Note already used would lead to the result that the value of $E_1 + E_2 + E_3$ is independent of the choice of axes (just as was $e_1 + e_2 + e_3$ in the discussion of equations (3) and its results). Since, with the choice of the principal axes of strain, the values of the E_{rs} are as stated above, it follows that

$$E_1 + E_2 + E_3 = (r_2r_3)^2 + (r_3r_1)^2 + (r_1r_2)^2,$$

which is just equation (15). The details of the proof of these statements are not difficult to supply, but for our purpose it is the result (18) which is important.

As a final step in the elucidation of Gibbs, I, pages 205–211 we shall now adopt Gibbs' plan of allowing the axes to which we refer the system in its strained state to be any set of orthogonal axes OX, OY, OZ, not necessarily coincident with OX', OY', OZ'. Referred to these axes the coordinates of P'' are x, y, z and those of Q'' are $x + \xi$, $y + \eta$, $z + \zeta$, so that the local coordinates of Q'' in a set of local axes through P'' parallel to OX, OY, OZ are ξ, η, ζ. The procedure now can be practically copied from the previous pages. Let us use a symbolism similar to that employed above, and write

$$a_{11} \text{ for } \frac{\partial x}{\partial x'}, \quad a_{12} \text{ for } \frac{\partial x}{\partial y'}, \quad a_{21} \text{ for } \frac{\partial y}{\partial x'}, \quad \text{etc.} \ldots$$

Then we find that

$$\left.\begin{aligned} \xi &= a_{11}\xi' + a_{12}\eta' + a_{13}\zeta', \\ \eta &= a_{21}\xi' + a_{22}\eta' + a_{23}\zeta', \\ \zeta &= a_{31}\xi' + a_{32}\eta' + a_{33}\zeta'. \end{aligned}\right\} \tag{21}$$

It follows that

$$\overline{P''Q''}^2 = a_1\xi'^2 + a_2\eta'^2 + a_3\zeta'^2 + 2a_4\eta'\zeta' + 2a_5\zeta'\xi' + 2a_6\xi'\eta', \tag{22}$$

where

$$\left.\begin{aligned} a_1 &= a_{11}^2 + a_{21}^2 + a_{31}^2, \\ a_2 &= a_{12}^2 + a_{22}^2 + a_{32}^2, \\ a_3 &= a_{13}^2 + a_{23}^2 + a_{33}^2, \\ a_4 &= a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33}, \\ a_5 &= a_{13}a_{11} + a_{23}a_{21} + a_{33}a_{31}, \\ a_6 &= a_{11}a_{12} + a_{21}a_{22} + a_{31}a_{32}. \end{aligned}\right\} \tag{23}$$

Now although a_{11}, a_{12}, a_{21}, etc., are not respectively the same as e_{11}, e_{12}, e_{21} etc. (unless of course OX, OY, OZ should coincide with OX', OY', OZ'), nevertheless a comparison of (8) and (22), which are true for any values of ξ', η', ζ', shows that

$$a_1 = e_1, \quad a_2 = e_2, \quad a_3 = e_3, \quad a_4 = e_4, \quad a_5 = e_5, \quad a_6 = e_6.$$

In consequence of (11), therefore,

$$\left.\begin{aligned} a_1 + a_2 + a_3 &= r_1^2 + r_2^2 + r_3^2, \\ a_2a_3 + a_3a_1 + a_1a_2 - a_4^2 - a_5^2 - a_6^2 & \\ &= r_2^2r_3^2 + r_3^2r_1^2 + r_1^2r_2^2, \\ \begin{vmatrix} a_1 & a_6 & a_5 \\ a_6 & a_2 & a_4 \\ a_5 & a_4 & a_3 \end{vmatrix} &= r_1^2r_2^2r_3^2. \end{aligned}\right\}. \tag{24}$$

Just as before, we recognize that the determinant in (24) is the square of the determinant

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}, \tag{25}$$

and this is actually the determinant indicated by H in Gibbs, while the one in (24) is there indicated by G. Hence equations [437] and [442] are included in (24) and (25). We have been using a double suffix and single suffix notation as the most convenient to follow in this exposition and the most consistent with present day practice, but for comparison with Gibbs' treatment the reader will observe that A, B, C, a, b, c defined by him in [418] and [419] are respectively $a_1, a_2, a_3, a_4, a_5, a_6$ in this exposition. A glance shows that the first of equations (24) is the first of the equations [439]. The second of (24) is, as before, a little more troublesome to deal with by straightforward algebra, but it can be verified that the expression on the left hand side is the sum of the squares of the nine first minors of the determinant (25). A similar notation for these minors can be introduced as before, viz., A_{11} for the minor of a_{11}, A_{12} for that of a_{12}, A_{21} for that of a_{21}, etc. Thus the equations (24) can be written

$$\left.\begin{aligned} &\sum_r \sum_s a_{rs}^2 = r_1^2 + r_2^2 + r_3^2, \\ &\sum_r \sum_s A_{rs}^2 = (r_2 r_3)^2 + (r_3 r_1)^2 + (r_1 r_2)^2, \\ &\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}^2 = r_1^2 r_2^2 r_3^2. \end{aligned}\right\} \tag{26}$$

The left hand side of the first of these is the expression denoted by E in Gibbs; the expression on the left hand side of the second is referred to as F (see [432] and [434]), and, as already mentioned, H is used for the determinant in (25) and G for the determinant in (24). Thus equations (26) are just the set [439]. Again pursuing a line of argument such as led to (18) we obtain

$$\left.\begin{aligned} K\alpha &= K'(A_{11}\alpha' + A_{12}\beta' + A_{13}\gamma'), \\ K\beta &= K'(A_{21}\alpha' + A_{22}\beta' + A_{23}\gamma'), \\ K\gamma &= K'(A_{31}\alpha' + A_{32}\beta' + A_{33}\gamma'), \end{aligned}\right\} \qquad (27)$$

where K and α, β, γ are the area and direction cosines of the normal after the strain for a bounded plane surface (referred to OX, OY, OZ) whose area and direction cosines are given by K', α', β', γ' in the unstrained state (referred to OX', OY', OZ'). As already stated these results are of importance on pages 192, 193 of Gibbs' discussion.

3. Heterogeneous Strain. In the discussion just completed x, y, z have been considered as linear functions of x', y', z', with the result that the a_{rs} quantities (i.e., $\partial x/\partial x'$, etc.) are constants throughout the system, and the same remark applies to the A_{rs} quantities (viz., $(\partial y/\partial y')\,(\partial z/\partial z') - (\partial y/\partial z')\,(\partial z/\partial y')$, etc.). If, however, the displacements of the points from the unstrained to the strained states have such values that x, y, z are not linear functions of x', y', z', then the quantities denoted by a_{rs} are *functions of* x', y', z' varying from point to point, and the same is true for the quantities denoted by A_{rs} and also for the determinant denoted by the symbol H in Gibbs. (The flexure or the torsion of a bar are examples of heterogeneous strain.) As far as interpretation is concerned these functions still determine the various ratios of enlargement, with the understanding that the values of these functions at a given point give the necessary data for calculating the conditions of strain in a physically small element of volume surrounding the point. In short, we regard the strain as homogeneous throughout any physically small element of volume, giving the various a_{rs} and A_{rs} quantities the values throughout this element which they have at its central point.

4. Analysis of Stress. In using such a phrase as "the system in its unstrained state" we implicitly assume that we shall take this state as one in which the internal actions and reactions between any two parts of the body shall be *regarded* as vanishing. When we begin to consider if such actions are really zero, we are facing the very difficult physical problem of explaining by what mechanism such actions are exerted. We may imagine that an elastic medium is free from everything in the nature of external force, even gravity; we can hardly say, in view of the customary notions of molecules and intermolecular forces, that across the surface which separates two parts of the medium no forces are exerted. Therefore in using the word "stress" as a general term for the actions and reactions across dividing surfaces *which accompany strain* and vanish when the strain vanishes, we must regard stress as referring to *change* in the integral of the intermolecular forces exerted across some finite portion of such a surface, if we adopt a molecular theory of the constitution of matter. However, in thermodynamical reasoning we avoid the use of such conceptions, and we take it as a fundamental assumption, well backed by experience, that there is for any solid or fluid medium a condition of equilibrium to which the system can be brought which can be termed conventionally the unstrained state, and from which the medium can be strained by the application of external forces, this process giving rise to reciprocal internal forces across any conceptual surface dividing the medium into two parts. Of such external forces the most obvious example is gravity. This is sometimes referred to as a "body force," being proportional to the mass of each element of volume considered as pulled by the earth, moon, sun, etc. Other types of external forces are the thrusts on the surface of a body exerted by some liquid or gaseous medium surrounding it, or on certain parts of the surface by a solid body in contact with it. The pulls exerted by chains, ropes, etc., may be considered as body forces exerted throughout small parts of the body; e.g., if a pull is exerted by means of a string fastened to a nail embedded in the body, we can regard the medium as actually existing throughout the small hole made by the nail, and a body force existing in that small volume. Or alternatively they might be regarded as surface pulls exerted across a definite small portion of the bounding surface of the body. If a body is electrified or magnetized the forces exerted by external magnets and conductors, charged or conveying current, are also external forces. Such external forces must be clearly distinguished from the *stresses* which are occasioned by them. To give a definition of the "stress at a point," we must conceive a surface, on which the point lies, dividing the body into two parts. We also conceive a small element of this surface surrounding this point. Of the total force which we imagine one portion of the body to exert on the other across this surface, a certain small part is considered to be exerted across this element and, when the element is small enough in size, to be practically proportional in magnitude to the area of the element and unchanged in direction as the element is made smaller and smaller. The quotient of this force by the area is assumed to have a limiting value as both are indefinitely diminished in magnitude. The reader is certainly acquainted with this conception in the case of liquids and gases; but in such a case there is a special simplification. For one thing the force is almost always in the nature of a thrust in a fluid medium; in a solid medium it may be a thrust or a pull. Moreover, in the case of a fluid at rest, the force is normal to the element of the conceptual surface. That is not in general the case for solid media. The limiting value of the quotient of force by area referred to above is called the stress across the surface at the point, and, as stated, it is not as a rule directed along the normal to the surface at the point. Another important distinction should be noted here. In the case of a fluid not only is the pressure always normal to the element, but it retains the same value as the element assumes different orientations. (If the reader has forgotten the proof of this it would do no harm if he refreshed his memory, as the proof involves some considerations of value to us presently). But in the case of a solid medium the stress generally alters in value, as well as direction, as the orientation of the element of surface is changed. In the technical language of the vector calculus, the stress is a vector function of the unit vector which is normal to the element and changes in magnitude and direction as the unit vector is turned to be in different directions. In the case of a fluid medium at rest one numerical magnitude is obviously all that is required to specify the pressure at a point, and the physical problems raised involve the functional dependence of this pressure on the position of the point. But for a solid medium the conditions are more complex, and we must consider carefully just how many numerical magnitudes must be given in order to specify the stress at a point, i.e., to indicate what is the stress at the point across any assigned element of surface. We shall see presently that there are six, and, as is readily suggested by the example of a fluid, each of these may vary in value with the position of the point, i.e., be a function of the coordinates of the point. The analysis of the stress at a point proceeds as follows.

Consider the point P, the displaced position of a point P' in the unstrained state, and let its coordinates referred to the axes OX, OY, OZ (chosen for the strained state) be x, y, z.* First let the conceptual dividing surface be parallel to OYZ, i.e., a plane surface at right angles to OX. We can resolve the postulated force across the element of area at P into three components parallel to the axes, and these *when divided by the area of the element* we denote by X_X, Y_X, Z_X, the suffix indicating clearly that the plane surface under consideration is normal to OX. X_X is of the nature of a tension or pressure, while Y_X and Z_X are "shearing tractions," their directions lying in the dividing surface. Of course each of these in general varies in value with the position of P and so should strictly be written as

$$X_X(x, y, z),\ Y_X(x, y, z),\ Z_X(x, y, z)$$

to indicate their functional dependence on the values of x, y, z; however, for brevity, we drop the bracketed letters, but this point should never be lost sight of. By considering plane surfaces containing P normal to OY and OZ we can introduce components of the forces at P across these surfaces, when divided by the area of the element, as X_Y, Y_Y, Z_Y and X_Z, Y_Z, Z_Z. By the aid of these nine quantities we can now express the stress at P across any element of surface containing P whose direction cosines are given, say α, β, γ. To do so, draw local axes at P (Fig. 5) and let a plane surface whose direction cosines are α, β, γ cut them in the points Q, R, S. Let K be the area of the triangle QRS; then $K\alpha$ is the area of the triangle PRS, $K\beta$ of PSQ and $K\gamma$ of PQR. The portion of the medium within the tetrahedron $PQRS$ is in equilibrium under the body forces on it and the stress actions on it across the four triangles mentioned. Let us enumerate the latter first. Parallel to OX we have a force across PRS of amount $-K\alpha X_X$. (We are assuming that X_X is positive if it is a tension, and negative if a pressure; also that the tetrahedron $PQRS$ lies in the positive octant, i.e., the octant for which the local coordinates ξ, η, ζ are all positive). Also parallel to OX we have a force $-K\beta X_Y$ (a tangential shearing force) across PSQ, and across PQR a force $-K\gamma X_Z$ (also shearing). In considering the equilibrium we can, if we gradually reduce the size of the tetrahedron, neglect the body forces on it in comparison with the surface forces just enumerated. The point involved is the same as that introduced in elementary treatises on hydrostatics when proving the uniformity of fluid pressure in all directions, and will doubtless be known to the reader, or easily looked up. (Actually it only requires us to remember that the body forces involve the product of a finite quantity and the volume, while a surface action involves the product of a finite quantity and an area. As the size of the tetrahedron diminishes, the magnitude of the volume becomes very small in comparison with the magnitude of the surface, since the former involves the cube of a small

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* We may from this point onwards drop double accents in symbols for strained positions and coordinates as no longer necessary.

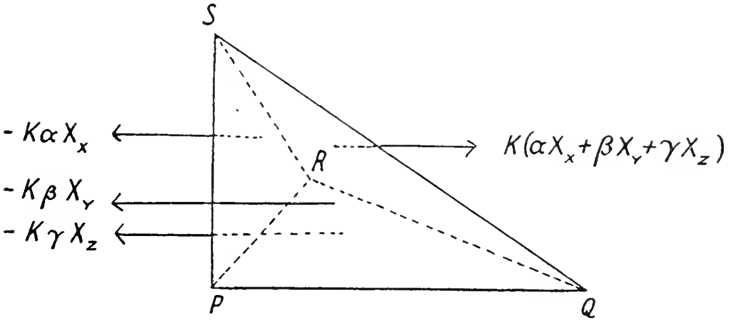

FIG. 5

length and the latter the square.) It follows that if equilibrium exists the component of force across the surface QRS parallel to OX is, for a small value of K, practically equal to

$$K(\alpha X_X + \beta X_Y + \gamma X_Z).$$

The quotient of this force by the area K is the x-component of the stress at P across the plane (α, β, γ) (meaning the plane whose normal has these direction cosines). Similar results can be obtained for the other components, and we arrive at the result that the stress across the plane (α, β, γ) has the components

$$\left.\begin{array}{c}\alpha X_X + \beta X_Y + \gamma X_Z, \qquad \alpha Y_X + \beta Y_Y + \gamma Y_Z, \\ \alpha Z_X + \beta Z_Y + \gamma Z_Z.\end{array}\right\} \tag{28}$$

We know that in fluid media in equilibrium the pressure varies with the depth owing to the action of gravity, and in general the pressure at a point varies with the position of the point when body forces are exerted on the fluid. The reader may be acquainted with the relation between the "gradient of the pressure" (i.e., the rate of variation of pressure per unit of distance in a given direction) and the body force. It is dealt with in works on hydromechanics and is given by the equations

$$\frac{\partial p}{\partial x} = F_X, \quad \frac{\partial p}{\partial y} = F_Y, \quad \frac{\partial p}{\partial z} = F_Z,$$

where F_X, F_Y, F_Z are the components of the force F *on unit volume* of the fluid. Moreover, if at any point on the surface of the fluid there is an external force in the nature of a thrust or pull on the surface, and if F is the value of it per unit surface at the point, then the value of the pressure at that point of the surface is given by

$$\alpha p = -F_x, \quad \beta p = -F_y, \quad \gamma p = -F_z,$$

where α, β, γ are the direction cosines of the outwardly directed normal to the surface at the point. By exactly the same type of reasoning which leads to this result, we can find relations between the body forces on a solid body and the space differential coefficients of the "stress constituents" X_X, X_Y, ... Z_Z.

To obtain them we visualize a very small rectangular parallelopiped (Fig.6) of the medium *in the state of strain* which has the point P at its center. It is bounded by six rectangular faces parallel in pairs to the planes of reference OYZ, OZX, OXY. The local axis of x through P cuts one face parallel to OYZ in a point Q and the other in a point U, such that $PQ = PU = \xi$, the coordinates of Q being $x + \xi, y, z$ and of $U, x - \xi, y, z$. The local axes of y and z each cut two faces, in the points R, V and S, W, respectively, RV being equal to 2η, and SW to 2ζ. Thus the volume of the parallelopiped is $8\xi\eta\zeta$, its sides being 2ξ, 2η, 2ζ and its faces having the areas $4\eta\zeta$, $4\zeta\xi$, $4\xi\eta$. Let $X_X, \ldots Z_Z$ be the values of the "stress-constituents" at P. At Q they are

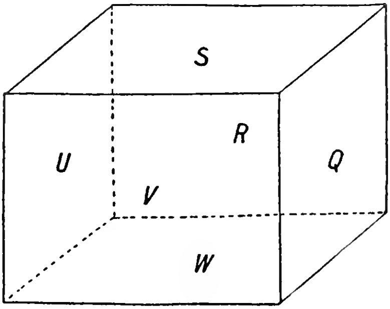

FIG. 6

$$X_X + \frac{\partial X_X}{\partial x}\xi, \qquad X_Y + \frac{\partial X_Y}{\partial x}\xi, \qquad \ldots, \qquad Z_Z + \frac{\partial Z_Z}{\partial x}\xi.$$

At U they are

$$X_X - \frac{\partial X_X}{\partial x}\xi, \qquad X_Y - \frac{\partial X_Y}{\partial x}\xi, \qquad \ldots, \qquad Z_Z - \frac{\partial Z_Z}{\partial x}\xi,$$

and similar formulae give the values at R, V, S, W. If we assume the values at Q to be the average values over the face containing Q, then the medium outside the parallelopiped exerts a pull on it across this face in the direction of OX of amount

$$\left(X_X + \frac{\partial X_X}{\partial x}\xi\right) 4\eta\zeta,$$

since $4\eta\zeta$ is the area of this face. Across the face containing U there will be a pull *in the opposite direction* XO of amount

$$\left(X_X - \frac{\partial X_X}{\partial x}\,\xi\right) 4\eta\zeta.$$

The difference of these, viz.,

$$\frac{\partial X_X}{\partial x} \cdot 8\xi\eta\zeta$$

is the resultant of these two in the direction OX. To proceed, we also have a shearing force on the parallelopiped in the direction OX of amount

$$\left(X_Y + \frac{\partial X_Y}{\partial y}\,\eta\right) 4\zeta\xi$$

across the face containing R, and one of amount

$$\left(X_Y - \frac{\partial X_Y}{\partial y}\,\eta\right) 4\zeta\xi$$

across the face containing V in the direction XO. These two forces yield a resultant

$$\frac{\partial X_Y}{\partial y}\, 8\xi\eta\zeta$$

in the direction OX. The remaining pair of faces contribute a resultant force in the direction of OX of amount

$$\frac{\partial X_Z}{\partial z}\, 8\xi\eta\zeta.$$

Thus the stress actions exerted by the surrounding medium on the parallelopiped are equivalent to a force whose x-component is

$$\left(\frac{\partial X_X}{\partial x} + \frac{\partial X_Y}{\partial y} + \frac{\partial X_Z}{\partial z}\right) 8\xi\eta\zeta.$$

The resultant body force arising from external influences on the parallelopiped we represent by the symbol F, *estimated per unit volume,* so that the x-component of this on the element of volume we are considering is $F_X \cdot 8\xi\eta\zeta$. Since the medium is in equilibrium, the sum of the components in any direction of all the forces on an element of volume (including those due to influences external to the medium and those arising from the part of the medium surrounding the element) is zero, and therefore

$$\frac{\partial X_X}{\partial x} + \frac{\partial X_Y}{\partial y} + \frac{\partial X_Z}{\partial z} + F_X = 0.$$

In just the same manner we can prove that

$$\left.\begin{aligned} \frac{\partial Y_X}{\partial x} + \frac{\partial Y_Y}{\partial y} + \frac{\partial Y_Z}{\partial z} + F_Y = 0, \\ \frac{\partial Z_X}{\partial x} + \frac{\partial Z_Y}{\partial y} + \frac{\partial Z_Z}{\partial z} + F_Z = 0. \end{aligned}\right\} \qquad (29)$$

The equations [377] constitute a particular case of these; for the forces arising from gravity have no horizontal components and, since in Gibbs OZ is in the vertically upward direction, F_Z is his $-g\Gamma$.

If at the surface there are external forces in the nature of thrusts or pulls on it, and if at any point such an external force is represented by F estimated per unit area (regarded as positive if it is a pull), then at the surface we also have the equations

$$\left.\begin{aligned} \alpha X_X + \beta X_Y + \gamma X_Z &= F_x, \\ \alpha Y_X + \beta Y_Y + \gamma Y_Z &= F_y, \\ \alpha Z_X + \beta Z_Y + \gamma Z_Z &= F_z, \end{aligned}\right\} \qquad (29a)$$

where α, β, γ are the direction cosines of the outwardly directed normal to the surface at the point. This follows from the consideration that a thin layer of matter at the surface of the body exerts on the matter in the interior a stress-action per unit area, whose component parallel to OX is $\alpha X_X + \beta X_Y + \gamma X_Z$, etc. Hence the interior matter exerts on this thin layer an action whose x-component per unit area is $-(\alpha X_X + \beta X_Y +$

γX_Z). For equilibrium the sum of this and F_x, the external surface force-component per unit area, must be zero.

It was stated that the stress at a point was determined by six independent quantities, but so far we seem to have reduced it to a representation by nine. So we shall now turn our attention to three relations which exist between these nine constituents, and which are given in [375] and [376], proving these, however, by a more direct and more easily grasped method than that employed by Gibbs. To this end let us once more give our attention to the conditions controlling the equilibrium of the parallelopiped (Fig. 6), and recall the fact that not only must the total resultant force on the parallelopiped vanish, but also the total couple as well. This couple is obtained by taking moments about the point P, and has three components, one around the local axis of x through P, one around the local axis of y, and one around the local axis of z. Consider the contributions made by each influence on the parallelopiped to the component of the total couple round the local axis of x. The pulls across the faces involving the constituents X_X, Y_Y, Z_Z are symmetrical with regard to P and contribute nothing to the couple. On the other hand the individual shearing forces obviously tend to produce twists. Those that tend to twist the element around the local axis of x are the shearing forces parallel to the local axes of y and z, and they are the following four:

$$\left(Z_Y + \frac{\partial Z_Y}{\partial y}\eta\right) 4\zeta\xi \text{ across the face containing } R,$$

$$-\left(Z_Y - \frac{\partial Z_Y}{\partial y}\eta\right) 4\zeta\xi \text{ across the face containing } V,$$

$$\left(Y_Z + \frac{\partial Y_Z}{\partial z}\zeta\right) 4\xi\eta \text{ across the face containing } S,$$

$$-\left(Y_Z - \frac{\partial Y_Z}{\partial z}\zeta\right) 4\xi\eta \text{ across the face containing } W.$$

The moment of the first about the local axis of x is

$$\eta \cdot \left(Z_Y + \frac{\partial Z_Y}{\partial y}\eta\right) 4\zeta\xi$$

in a right-handed sense; that of the second is

$$\eta \cdot \left(Z_Y - \frac{\partial Z_Y}{\partial y}\eta\right) 4\zeta\xi$$

also in a right-handed sense. That of the third is

$$\zeta \cdot \left(Y_Z + \frac{\partial Y_Z}{\partial z}\zeta\right) 4\xi\eta$$

in a left-handed sense and that of the fourth is

$$\zeta \left(Y_Z - \frac{\partial Y_Z}{\partial z}\zeta\right) 4\xi\eta$$

also in a left-handed sense. Thus the four shearing tractions yield a couple around the local axis of x in the right-handed sense of amount

$$8\xi\eta\zeta(Z_Y - Y_Z).$$

Turning now to the body forces we see that even if their action on the element is not symmetrical about P (as would be the case for example with gravity forces) they can yield in comparison with the moments arising from the shearing forces only a vanishingly small couple, since about the local axis of x, for instance, this couple must have an order of magnitude which cannot be greater than the product of F_Y, $8\xi\eta\zeta$ and ζ, or F_Z, $8\xi\eta\zeta$ and η. Since $\xi\eta\zeta^2$ or $\xi\eta^2\zeta$ is small compared to $\xi\eta\zeta$ when ξ, η and ζ are small, these contributions are evanescent in comparison with that written above, when the volume considered is small. Thus the total couple on the parallelopiped has components around the three axes given by

$$(Z_Y - Y_Z)8\xi\eta\zeta, \qquad (X_Z - Z_X)8\xi\eta\zeta, \qquad (Y_X - X_Y)8\xi\eta\zeta.$$

But in equilibrium these components must be zero, and so

$$Y_Z = Z_Y, \qquad Z_X = X_Z, \qquad X_Y = Y_X. \tag{30}$$

This demonstrates that there are only six independent strain-constituents, as already stated.

It must not be forgotten that this analysis relates to any arbitrary choice of axes of reference. Actually it is possible, by selecting a special triad of orthogonal lines as axes, to introduce a diminution in the number of stress-constituents required for the formulation of the stress across any given plane at a given point. A proof of this statement appears in Gibbs, I, 194, 195, but it is not so familiar and not so easy to grasp as the usual proof given in works on elasticity, which follows a line of reasoning similar to that adopted earlier to indicate the existence of three principal axes of strain, and is here outlined.

Conceive that a quadric surface whose equation is

$$X_X\xi^2 + Y_Y\eta^2 + Z_Z\zeta^2 + 2Y_Z\eta\zeta + 2Z_X\zeta\xi + 2X_Y\xi\eta = k$$

is constructed with P as center and with any local axes of reference at P; $X_X, X_Y, \ldots Z_Z$ being the values of the stress constituents at the point P. Let a line whose direction cosines are α, β, γ be drawn from P cutting this quadric in the point Q; denote the length of PQ by r so that the local coordinates of Q are $r\alpha$, $r\beta$, $r\gamma$. Now draw the tangent plane at Q to the quadric surface and drop PN perpendicular to this plane. By the theorem already used we know that the equation of this tangent plane is

$$(X_Xr\alpha + X_Yr\beta + X_Zr\gamma)\xi + (Y_Xr\alpha + Y_Yr\beta + Y_Zr\gamma)\eta \\ + (Z_Xr\alpha + Z_Yr\beta + Z_Zr\gamma)\zeta = k$$

(remembering that $Y_Z = Z_Y$, etc.), and so the direction cosines of PN are proportional to

$$\alpha X_X + \beta X_Y + \gamma X_Z, \qquad \alpha Y_X + \beta Y_Y + \gamma Y_Z, \\ \alpha Z_X + \beta Z_Y + \gamma Z_Z.$$

Thus a glance at (28) shows us that the stress action at P across a plane normal to PQ is itself parallel to PN. In general PN is not coincident with PQ, i.e., the stress action across any plane is in general not normal to the plane, as we know already; but the information now before us about its direction indicates that there are three special orientations of the plane for which this happens to be true and for which PN lies along PQ. They are clearly the three principal planes of the quadric surface whose equation has been written down above. Were we to choose as axes of reference the three principal axes of this quadric, we know that the equation would only involve terms in ξ^2, η^2, ζ^2, but not in $\eta\zeta$, $\zeta\xi$, $\xi\eta$. In short, with such a choice of axes of reference only three of the stress-components would have a finite value, viz., those corresponding to X_X, Y_Y, Z_Z. The remaining six (actually only three) would be zero, and as Gibbs states in equation [392] the stress action across any plane (α, β, γ) would have as its components αX_X, βY_Y, γZ_Z. These three special axes are called the *principal axes of stress*, and their existence is a point of considerable importance in the discussion in Gibbs, I, 195 *et seq.*

Special cases arise if the quadric surface at a point referred to above is one of revolution, i.e., if the section by one of the principal planes is a circle. In this event, assuming that it is the plane perpendicular to that one of the principal axes of stress designated as OX, it is clear that $Y_Y = Z_Z$, and the stress action across any plane containing the local axis of x at P is normal to this plane. Or it may happen that the "stress-quadric" is actually a sphere, so that $X_X = Y_Y = Z_Z$. Any triad of perpendicular lines will serve as principal axes of stress if this be so, and the stress-components which do not vanish have one numerical value, the stress across *any* plane being normal to it and having a value independent of direction. This is in fact the general state of affairs for a fluid *at rest* and $X_X = Y_Y = Z_Y = -p$ where p is the fluid pressure. It is clear that the equations of equilibrium (29) then degenerate to those for a fluid quoted on page 422.

5. *Stress-Strain Relations and Strain-Energy.* We have now considered at some length the mathematical methods by which the strains and stresses in a body are analyzed into their most convenient constituents, and it is clear that the differences of behavior observed in various elastic media when subject to given external forces arise from the different "constitutive" relations which exist between the constituents of stress and the coefficients of strain in these different media. We know for instance that the same pull will elongate a wire of brass of given section

and one of steel of the same section in different ratios; in both cases the X_x stress constituent is the same, but the e_{11} strain coefficient is different (the axis of x being supposed to be directed along the length of the wire). Obviously any complete theory would place at the disposal of the investigator the means of calculating in any given case, the strains which result from the imposition of definite external forces. Equations (29) are differential equations which connect the external forces with the stresses, so that with sufficient knowledge of these forces and of the state of stress at the surface of a body we can in theory determine the stress at any other point of the body. But this will not lead to a knowledge of the *strains* at each point unless we have a sufficient number of algebraic equations connecting the stress-constituents with the strain-coefficients. So far we have relied on the mathematician to develop the right conceptions and deduce the correct differential equations; we now have to turn to the experimenter who by subjecting each material to suitable tests determines the various "elastic constants" of any given substance. This is a matter on which little can be said here, but provided the tests do not strain a body beyond the limits from which it will return to its former condition without any "set" on removing the external forces, it is found, as a matter of experience, that there is approximately a linear relation between strain-coefficients and stress-constituents. *Under these conditions* the deformation of solid media is relatively so small that, although a rectangular element is in general after the strain deformed to an oblique parallelopiped, the various angles have been sheared from a right angle by relatively small amounts, and we can use the coefficients e_{11}, $e_{12}, \ldots e_{33}$, referring the system to the same axes before and after the strain. As we have seen above, the pure strains depend actually on six quantities, e_{11}, e_{22}, e_{33}, $e_{23} + e_{32}$, $e_{31} + e_{13}$, $e_{12} + e_{21}$, as the rotations are not a matter of importance; furthermore there are only six numerically different values involved in the nine quantities $X_x, .. Z_z$. Let us therefore introduce for convenience a small modification of the symbolism, and write

X_1 for X_X,	f_1 for $e_{11} - 1$,
X_2 for Y_Y,	f_2 for $e_{22} - 1$,
X_3 for Z_Z,	f_3 for $e_{33} - 1$,
X_4 for Y_Z or Z_Y,	f_4 for $e_{23} + e_{32}$,
X_5 for Z_X or X_Z,	f_5 for $e_{31} + e_{13}$,
X_6 for X_Y or Y_X,	f_6 for $e_{12} + e_{21}$.

(f_1, f_2, f_3 are the fractions of elongation along the axes and f_4, f_5, f_6 are the shears or changes in the angles between the axes.) A complete experimental knowledge of the elastic properties of any material would therefore be embodied in the ascertained values of the 36 elastic constants c_{rs} in six constitutive "stress-strain" equations such as

$$\left.\begin{aligned} X_1 &= c_{11}f_1 + c_{12}f_2 + c_{13}f_3 + c_{14}f_4 + c_{15}f_5 + c_{16}f_6, \\ X_2 &= c_{21}f_1 + c_{22}f_2 + c_{23}f_3 + c_{24}f_4 + c_{25}f_5 + c_{26}f_6, \end{aligned}\right\} \qquad (31)$$

and four similar equations. These equations are the expression of a general Hooke's law, a natural extension of the famous law concerning extension of strings and wires due to that English natural philosopher.

This apparently presents an appallingly complex problem for the experimental physicist; however, there are important simplifications in practice. To begin with, it will appear from energy considerations to be discussed presently, that even in the most general case the 36 constants must only involve 21 different numerical values at most, and actually for a great variety of materials still further reductions are involved. Indeed, for isotropic bodies all the elastic constants of such a material are calculable from the numerical values of two "elastic moduli," the well-known "bulk modulus" (or "elasticity of volume") and the "modulus of rigidity." For various crystalline bodies conditions of symmetry also involve a material reduction of the number of independent constants below the number 21.

The two moduli for isotropic bodies are referred to by

Gibbs and perhaps merit a brief remark here. When a body is subject to a uniform stress in all directions we have

$$X_X = Y_Y = Z_Z$$

and

$$X_Y = Y_X = Y_Z = Z_Y = Z_X = X_Z = 0.$$

If the body is isotropic, then referred to any axes

$$e_{11} = e_{22} = e_{33}$$

and

$$e_{12} = e_{21} = e_{23} = e_{32} = e_{31} = e_{13} = 0.$$

Thus along any line there is a fraction of elongation f, where $f = e - 1$, e being the common value of e_{11}, e_{22}, e_{33}. Hence the fraction of dilatation of volume is $e^3 - 1$ or practically $3f$. The quotient of the common value of X_X, Y_Y, Z_Z by $3f$ is called the bulk-modulus. (Gibbs calls it "elasticity of volume" on page 213.) The conception is most important in the case of a fluid. Here a variation of external thrust on the surface produces a variation of pressure from p to $p + \delta p$; there results from this an alteration of volume from v to $v + \delta v$ (δv is essentially negative if δp is essentially positive), i.e., a fraction of dilatation $\delta v/v$. The bulk-modulus is the limit of $-\delta p/\frac{\delta v}{v}$; i.e., it is

$$-v\frac{\partial p(v, t)}{\partial v},$$

where $p(v, t)$ is the function connecting pressure with volume and temperature. (See [448].) This definition is synonymous with the previous one, since for a liquid $p = -X_X = -Y_Y = -Z_Z$ and the shearing stresses vanish. (In fact the state of stress uniform in all directions, mentioned above, is often referred to as the case of "hydrostatic stress".)

We can have a state of stress also in which the six constituents vanish except (say) Y_Z(or Z_Y). In this case, for an isotropic body, $f_1 = f_2 = f_3 = 0$ and also $f_5 = f_6 = 0$. Only f_4 is finite and for the case of Hooke's law varies directly as Y_Z. The quotient of Y_Z by f_4 is called the "modulus of rigidity," or simply the "rigidity" of the material. Of course one should bear in mind that the strains must be small if the physical facts are to be consistent with these definitions

We thus see that a given system of external forces on a body involves a determinate set of stress-constituents when the body is in equilibrium under the forces, and these in their turn by reason of the stress-strain relations (linear or otherwise) determine a definite condition of strain. Infinitesimal variations in the external forces change the stress infinitesimally to $X_1 + dX_1$, etc. in the new state of equilibrium, and the strain coefficients are altered to $f_1 + df_1$, etc., where $X_1 + dX_1$, etc. are connected with $f_1 + df_1$, etc. by the same six equations as before. Actually we can conceive that "in the neighborhood" of a given state of equilibrium involving a definite condition of strain there are an infinite number of other states, which are not necessarily equilibrium states, characterized by values $f_1 + \delta f_1$, etc. of the coefficients where the δf_r are entirely arbitrary, so that $f_1 + \delta f_1$, etc. are not connected with the external forces by means of the stress-strain relations. For further information on these matters the reader is referred to standard texts on elasticity and to R. W. Goranson's "*Thermodynamic Relations in Multi-component Systems*" (Carnegie Institution of Washington, Pub. No. 408, 1930).*

Our ultimate object in what has preceded is to lead up to the expression which represents the change in the energy of strain when the condition of strain has been altered by a change from a state of equilibrium to a neighboring state. This must be included in the expression for the total change of energy when we are formulating the first and second laws of thermodynamics. It is in fact the expression which is to replace

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* The reader must be careful to remember that the author's symbolism, which has been chosen to diverge as little as possible from that of Gibbs, differs in some details from that used in these references.

$-p\delta v$ in the law for a fluid medium

$$\delta\epsilon = t\delta\eta - p\delta v.$$

The natural method of procedure would be to consider the movements of the points of application of the external forces involved in the change of strain and, combining these with the forces themselves, to determine the work of the external forces; this work, if there is no exchange of heat, will be equal to the change in internal energy. Unfortunately this method involves the use of certain general theorems of mathematical analysis which may be unfamiliar to some readers and the writer will therefore make shift with a more elementary, if less rigorous, method.

We revert to our picture of an element of volume surrounding the point P in the state of strain determined by the values e_{11}, ... e_{33} of the strain-coefficients (see Fig. 6). The element is assumed to be strictly rectangular in this state (although not necessarily so in the state of reference); its sides are parallel to the axes OX, OY, OZ and have the elementary lengths h, k, l respectively. We conceive that this medium receives a further strain to the condition determined by $e_{11} + \delta e_{11}$, etc., and this involves infinitesimal elongations and shears in the rectangular element. We now imagine the element to be isolated and to experience the same movements under a set of external forces which are equal to the forces which we assume to exist across its faces when *in situ*. The work of these hypothetical forces we take to be the increase in strain-energy of the element. In the circumstances of the case e_{11}, e_{22}, e_{33} are near to unity in value, so that in comparison with them $e_{11} - 1$, $e_{22} - 1$, $e_{33} - 1$, e_{23}, e_{32}, e_{31}, e_{13}, e_{12}, e_{21}, as we noted earlier, are small. The rectangular element has had its side h elongated by a fraction δf_1. The matter surrounding the element is exerting on it forces across the kl faces equal to klX_X. Hence work is done which can be calculated by conceiving one of the kl faces fixed and the other moving a distance $h\delta f_1$ in the direction of the force klX_X. (The shearing forces klY_X and klZ_X across these faces are at right angles to the elongation and so this movement involves no work on their part.) This work is $hklX_X\delta f_1$, and this is therefore one part of the increase of energy in the element of volume. The other pairs of faces when treated similarly yield further parts of the energy increase, viz. $hklY_Y\delta f_2$ and $hklZ_Z\delta f_3$. Now let us turn to the shears and fix our attention for the moment on the faces of the element which are parallel to the plane OXY and are separated by the distance l in the direction of OZ. A little thought will show that one of these faces has moved in a shearing manner relatively to the other by an amount which is the vector sum of a component $l\delta(e_{31} + e_{13})$ parallel to OX and a component $l\delta(e_{23} + e_{32})$ parallel to OY. (A glance at equation (10) will remind the reader that the "shear" of lines parallel originally to OX and OZ is $\delta[e_5/(e_3e_1)^{\frac{1}{2}}]$ which is substantially $\delta(e_{31} + e_{13})$; the "shear" practically measures the small change in the (right) angle between OZ and OX.) We can again simplify our argument by conceiving one of the hk faces fixed and the other slipping over it by amount $l\delta f_5$ in the direction of OX. The shearing pull across this face by the surrounding matter in the element is hkX_Z in this direction. (The face is perpendicular to OZ and the pull is in the direction OX.) Thus the work done on this account is $hklX_Z\delta f_5$. Similar reasoning yields $hklY_Z\delta f_4$ for the other component. Each of the other pairs of faces treated in a similar manner would yield similar terms; the faces parallel to OYZ would yield $hklY_X\delta f_6$ and $hklZ_X\delta f_5$, and the faces parallel to OZX would yield $hklZ_Y\delta f_4$ and $hklX_Y\delta f_6$. It would seem that in order to obtain the increase of energy associated with the shearing movements, we ought to add these six terms. This is, however, one of the pitfalls of this simple method which we are using so as to evade advanced analytical operations. If we adopted this procedure we should obtain twice the correct increase associated with the shears, and it is not difficult to realize that this is so. For a shear of one Z-face past the other Z-face (meaning the faces perpendicular to the direction OZ) in the direction parallel to OX involves of necessity a shear of an X-face past the other X-face in the direction parallel to OZ. Either shear is one of two alternative ways of describing the resulting distortion. Now our method of calculating the work done in this case really requires us to conceive the element of volume as isolated and sheared *either* by a shearing pull hkX_Z across a Z-face *or* a shearing pull klZ_X across an X-face. One way yields $hklX_Z\delta f_5$ for the work done; the other yields $hklZ_X\delta f_5$ for it; these are the same quantity since $Z_X = X_Z$, but we must not count both or we shall obtain twice the correct value, and this is just what we would be doing if we added all the terms obtained above. In this comparatively simple way we can reasonably assume a result which can be more rigorously established by other methods, viz., that when the strain of a solid is varied from a state in which the strain coefficients are $e_{11}, \ldots e_{33}$, to one in which the coefficients are $e_{11} + \delta e_{11}, \ldots e_{33} + \delta e_{33}$, the increase in energy in an element of volume is the product of the volume of the element and

$$X_1\delta f_1 + X_2\delta f_2 + X_3\delta f_3 + X_4\delta f_4 + X_5\delta f_5 + X_6\delta f_6. \quad (32)$$

This expression takes the place of the expression $-p\delta v$ for a fluid in the formulation of the variation of the internal energy of a solid body in any general change of temperature and state. That the expression (32) degenerates to this in the case of a fluid can be readily demonstrated, for we have seen earlier that in the case of a fluid X_4, X_5, X_6 are zero, and $X_1 = X_2 = X_3 = -p$; hence (32) becomes

$$-p\ \delta(f_1 + f_2 + f_3),$$

and, since unit volume expands in this case to

$$(1 + \delta f_1)\ (1 + \delta f_2)\ (1 + \delta f_3),$$

or practically

$$1 + \delta(f_1 + f_2 + f_3),$$

it follows that δv is equal to the original volume of the element multiplied by $\delta(f_1 + f_2 + f_3)$.

The whole of the argument so far has avoided any consideration of changes of temperature arising from strain and assumes all the energy to be mechanical. In so far as this is allowable the expression $X_1\delta f_1\ \ldots + X_6\delta f_6$ must be regarded as the variation of a function of the six quantities $f_1, \ldots f_6$, so that if we denote this "strain-energy function" by $W(f_1, \ldots f_6)$ it follows that

$$X_1 = \frac{\partial W}{\partial f_1}, \ \ldots \ X_6 = \frac{\partial W}{\partial f_6}.$$

If then each X_r is a linear function of $f_1, \ldots f_6$, as experiment shows to be approximately the case for isothermal small changes, it follows that W must be a quadratic function of the six variables $f_1, \ldots f_6$. Now such a quadratic can only involve 21 numerically different coefficients; thus

$$\begin{aligned} W = {} & \tfrac{1}{2}c_{11}f_1^2 \ldots\ldots\ldots\ldots + \tfrac{1}{2}c_{66}f_6^2 \\ & + c_{12}f_1f_2 \ldots\ldots\ldots + c_{16}f_1f_6 \\ & + c_{23}f_2f_3 \ldots\ldots + c_{26}f_2f_6 \\ & + c_{34}f_3f_4 \ldots + c_{36}f_3f_6 \\ & + c_{45}f_4f_5 + c_{46}f_4f_6 \\ & + c_{56}f_5f_6, \end{aligned}$$

and so it appears in assuming that the various stress-constituents satisfy equations such as

$$X_r = c_{r1}f_1 \ldots + c_{r6}f_6,$$

that

$$c_{rs} = c_{sr}.$$

This justifies the statement made above that in the cases where there are linear isothermal stress-strain relations, there are at most 21 elastic constants.

In the arguments that follow, however, we shall require no such restriction as to the nature of the relations between stress-constituents and the strain-coefficients. Actually these relations also involve the temperature. Moreover, if we are going to follow Gibbs' reasoning we shall have to realize his somewhat different treatment of the stress-constituents from that outlined above, which is the usual treatment. It arises from his endeavor to make the foundation of his arguments as wide as possible. He lays down no restriction that the state of reference shall be so near to that of the state of strain that a rectangular element is but little strained from that form in the changes which take place between the two states. His only proviso is that the differential coefficients $\partial x/\partial x'$, etc. shall not alter appreciably over molecular distances, i.e., that the strain is homogeneous within a physically small element of volume. Let us retrace the ground covered by the argument which we followed when dealing with the energy of strain. The rectangular element of volume *in the state of strain* has its center at a point P whose coordinates are x, y, z with reference to the OX, OY, OZ axes; this element was, in the state of reference, an oblique parallelopiped whose centre was at the point P' whose coordinates are x', y', z' with reference to the OX', OY', OZ' axes. Let the edges of the element in the state of strain be parallel to OX, OY, OZ, and following the course we used earlier let us call the mid-points of the faces perpendicular to OX, Q and U, so that the *local* coordinates of Q with reference to local axes of x, y, z at P are ξ, 0, 0, and of U are $-\xi$, 0, 0. Those of Q', the center of the corresponding face of the unstrained element, for the local axes of x', y', z' at P' are ξ', η', ζ' where, by equations (21),

$$\left.\begin{aligned} \xi &= a_{11}\xi' + a_{12}\eta' + a_{13}\zeta', \\ 0 &= a_{21}\xi' + a_{22}\eta' + a_{23}\zeta', \\ 0 &= a_{31}\xi' + a_{32}\eta' + a_{33}\zeta'. \end{aligned}\right\} \tag{33}$$

Now let the slight increase of strain take place which we considered above when we treated this problem in a more restricted manner; the point P is displaced to a neighboring point P_δ, say, while Q and U are displaced to neighboring points Q_δ and U_δ. The strain-coefficients are now $a_{11} + \delta a_{11}$, etc. The local coordinates of Q_δ with reference to local axes of x, y, z at P_δ are $\xi + \delta\xi$, $\delta\eta$, $\delta\zeta$ where

$$
\begin{aligned}
\xi + \delta\xi &= (a_{11} + \delta a_{11})\xi' + (a_{12} + \delta a_{12})\eta' + (a_{13} + \delta a_{13})\zeta', \\
\delta\eta &= (a_{21} + \delta a_{21})\xi' + (a_{22} + \delta a_{22})\eta' + (a_{23} + \delta a_{23})\zeta', \\
\delta\zeta &= (a_{31} + \delta a_{31})\xi' + (a_{32} + \delta a_{32})\eta' + (a_{33} + \delta a_{33})\zeta'.^*
\end{aligned}
$$

Hence

$$
\begin{aligned}
\delta\xi &= \delta a_{11}\cdot\xi' + \delta a_{12}\cdot\eta' + \delta a_{13}\cdot\zeta', \\
\delta\eta &= \delta a_{21}\cdot\xi' + \delta a_{22}\cdot\eta' + \delta a_{23}\cdot\zeta', \\
\delta\zeta &= \delta a_{31}\cdot\xi' + \delta a_{32}\cdot\eta' + \delta a_{33}\cdot\zeta'.
\end{aligned}
$$

Now we need to express these variations in terms of ξ, and this is easily done; for, on solving equations (33) for ξ', η', ζ' in terms of ξ, we find that

$$
\begin{aligned}
\xi' &= \frac{A_{11}}{H}\,\xi, \\
\eta' &= \frac{A_{12}}{H}\,\xi, \\
\zeta' &= \frac{A_{13}}{H}\,\xi.
\end{aligned}
$$

where A_{rs} is the first minor (with its correct sign) of a_{rs} in the determinant H.

We write for convenience b_{rs} for A_{rs}/H, and in consequence we have the following three results

$$
\left.
\begin{aligned}
\delta\xi &= (b_{11}\delta a_{11} + b_{12}\delta a_{12} + b_{13}\delta a_{13})\xi, \\
\delta\eta &= (b_{11}\delta a_{21} + b_{12}\delta a_{22} + b_{13}\delta a_{23})\xi, \\
\delta\zeta &= (b_{11}\delta a_{31} + b_{12}\delta a_{32} + b_{13}\delta a_{33})\xi.
\end{aligned}
\right\} \qquad (34)
$$

It is easy to see that the coordinates of U_δ for the local axes at P_δ are just $-(\xi + \delta\xi)$, $-\delta\eta$, $-\delta\zeta$. Thus it appears that the rectangular element has had its edge parallel to OX elongated by $2\delta\xi$ i.e., by the fraction $(b_{11}\delta a_{11} + b_{12}\delta a_{12} + b_{13}\delta a_{13})$ of its length 2ξ. In short, $b_{11}\delta a_{11} + b_{12}\delta a_{12} + b_{13}\delta a_{13}$ is just the infinitesimal quantity δf_1 or δe_{11} which occurred in the previous treatment. Similarly the face containing Q has in this infinitesimal change of strain been sheared by an amount $2\delta\eta$ relatively to the opposite face containing U in the direction parallel to OY and by an amount $2\delta\zeta$ parallel to OZ. But as we have seen in the earlier treatment these shearing displacements are $\delta e_{21}\cdot 2\xi$ and $\delta e_{31}\cdot 2\xi$ respectively. Hence we find that

---

* Observe that P_δ and Q_δ are positions in the slightly altered state of strain of the *same* original points P', Q' in the state of reference.

$$\delta e_{21} = b_{11}\delta a_{21} + b_{12}\delta a_{22} + b_{13}\delta a_{23},$$

$$\delta e_{31} = b_{11}\delta a_{31} + b_{12}\delta a_{32} + b_{13}\delta a_{33}.$$

The other faces can be treated similarly and we thus arrive at the nine equations

$$\left.\begin{aligned}
\delta e_{11} &= b_{11}\delta a_{11} + b_{12}\delta a_{12} + b_{13}\delta a_{13},\\
\delta e_{22} &= b_{22}\delta a_{22} + b_{23}\delta a_{23} + b_{21}\delta a_{21},\\
\delta e_{33} &= b_{33}\delta a_{33} + b_{31}\delta a_{31} + b_{32}\delta a_{32},\\
\delta e_{23} &= b_{33}\delta a_{23} + b_{31}\delta a_{21} + b_{32}\delta a_{22},\\
\delta e_{32} &= b_{22}\delta a_{32} + b_{23}\delta a_{33} + b_{21}\delta a_{31},\\
\delta e_{31} &= b_{11}\delta a_{31} + b_{12}\delta a_{32} + b_{13}\delta a_{23},\\
\delta e_{13} &= b_{33}\delta a_{13} + b_{31}\delta a_{11} + b_{32}\delta a_{12},\\
\delta e_{12} &= b_{22}\delta a_{12} + b_{23}\delta a_{13} + b_{21}\delta a_{11},\\
\delta e_{21} &= b_{11}\delta a_{21} + b_{12}\delta a_{22} + b_{13}\delta a_{23}.
\end{aligned}\right\} \quad (35)$$

By our previous result the increase in the energy of the element of volume $8\xi\eta\zeta$ is equal to the product of $8\xi\eta\zeta$ and the expression

$$X_1\delta f_1 \ldots + X_6\delta f_6$$

or

$$X_X\,\delta e_{11} + Y_Y\,\delta e_{22} + Z_Z\,\delta e_{33} + Y_Z\,\delta e_{23} + Z_Y\,\delta e_{32} + Z_X\,\delta e_{31} + X_Z\,\delta e_{13} + X_Y\,\delta e_{12} + Y_X\,\delta e_{21}.$$

This by reason of the equations (35) becomes an expression such as

$$\tau_{11}\delta a_{11} + \tau_{12}\delta a_{12} + \tau_{13}\delta a_{13} + \tau_{21}\delta a_{21} + \text{etc.} \ldots + \tau_{33}\delta a_{33}, \quad (36)$$

where $\tau_{11}, \ldots \tau_{33}$ are nine linear functions of the stress-constituents $X_X, \ldots Z_Z$, involving the quantities b_{rs} in the coefficients. It will be found in fact that

$$\begin{aligned}\tau_{11} &= b_{11}X_X + b_{21}X_Y + b_{31}X_Z,\\ \tau_{12} &= b_{12}X_X + b_{22}X_Y + b_{32}X_Z,\\ \tau_{13} &= b_{13}X_X + b_{23}X_Y + b_{33}X_Z,\end{aligned}$$

and six similar equations. Now the expression (36) represents the change in the strain-energy caused by the infinitesimal increase of strain in the matter occupying unit of volume in the state of strain. But, as we have seen previously, this matter occcupies a volume H^{-1} in the state of reference, and so we must multiply the expression (36) by H in order to obtain the increase in strain energy of the matter which occupies *unit volume in the state of reference*. Now from the definition of b_{rs} given above we see that $b_{rs}H$ is equal to A_{rs}. Hence we arrive finally at the result that the infinitesimal increase in strain energy estimated *per unit of volume in the state of reference* is

$$\begin{aligned}&X_{X'}\delta a_{11} + X_{Y'}\delta a_{12} + X_{Z'}\delta a_{13}\\ &+ Y_{X'}\delta a_{21} + Y_{Y'}\delta a_{22} + Y_{Z'}\delta a_{23}\\ &+ Z_{X'}\delta a_{31} + Z_{Y'}\delta a_{32} + Z_{Z'}\delta a_{33},\end{aligned} \tag{37}$$

where

$$\left.\begin{aligned}X_{X'} &= A_{11}X_X + A_{21}X_Y + A_{31}X_Z,\\ X_{Y'} &= A_{12}X_X + A_{22}X_Y + A_{32}X_Z,\\ X_{Z'} &= A_{13}X_X + A_{23}X_Y + A_{33}X_Z,\\ Y_{Y'} &= A_{22}Y_Y + A_{32}Y_Z + A_{12}Y_X,\\ Y_{Z'} &= A_{23}Y_Y + A_{33}Y_Z + A_{13}Y_X,\\ Y_{X'} &= A_{21}Y_Y + A_{31}Y_Z + A_{11}Y_X,\\ Z_{Z'} &= A_{33}Z_Z + A_{13}Z_X + A_{23}Z_Y,\\ Z_{X'} &= A_{31}Z_Z + A_{11}Z_X + A_{21}Z_Y,\\ Z_{Y'} &= A_{32}Z_Z + A_{12}Z_X + A_{22}Z_Y.\end{aligned}\right\} \tag{38}$$

The expression (37) occurs in Gibbs' equation [355]. It is essentially his notation with the convenient simplification of replacing dx/dx' by a_{11}, etc.

It is really an important matter to realize that Gibbs' stress-constituents X_x', etc., are not to be confused with the stress-constituents X_x etc., of customary elastic solid theory. Gibbs himself gives on page 186 a physical signification to his constituents, which brings home to the careful reader how essential it is to be on guard when it is a question of giving a measure of a physical quantity *per unit of length or area or volume.* His own statement is so brief that for clarity it can be somewhat expanded. He asks us to consider an element of mass which *in the reference state* is rectangular (a "right parallelopiped" as he calls it) with its edges parallel to the axes OX', OY', OZ'. We shall adopt a method similar to that employed previously and regard the center of this at a point P', whose coordinates are x', y', z'. The middle points of the faces perpendicular to OX' shall be named Q' and U', the coordinates of Q' being $x' + \xi'$, y', z', and of U', $x' - \xi'$, y', z'; and so on. (The dx', dy', dz' of Gibbs are $2\xi'$, $2\eta'$, $2\zeta'$.) In the strained state the element is in general an oblique parallelopiped the center of which is at P, whose coordinates are x, y, z with reference to the new axes OX, OY, OZ. The coordinates of Q, the displaced position of Q', and still the center of one of the faces (now a parallelogram), are $x + \xi$, $y + \eta$, $z + \zeta$, where

$$\begin{aligned} \xi &= a_{11}\xi', \\ \eta &= a_{21}\xi', \\ \zeta &= a_{31}\xi'. \end{aligned}$$

(See equations (21), noting that the local coordinates of Q' in the local axes at P' are ξ', 0, 0.) Now consider a further infinitesimal displacement from this state in which only a_{11} varies, but not any of the other eight strain-coefficients. In such a variation ξ will alter by $\xi \cdot \delta a_{11}$ but η and ζ will not vary; i.e., the face we are considering will move further from the center of the element in the direction of OX (as Gibbs postulates in line 12 of page 186) by an amount $\xi' \cdot \delta a_{11}$. Similarly the face opposite will move relatively to the element's center an equal distance in the opposite direction; in other words one face will have separated from the other face by an amount $2\xi'\delta a_{11}$. Hence the work done by the components of the force on the element across these faces parallel to OX is equal to the product of $2\xi'\delta a_{11}$ and this force.

But a glance at (37), or [355] of Gibbs, shows us that, if no heat is imparted and only a_{11} varies, the increase in energy of the element is

$$X_{X'}\delta a_{11}\cdot 8\xi'\eta'\zeta'.$$

Hence as work done is equal to energy increase the force just referred to is $4\eta'\zeta' X_{X'}$, or $X_{X'}$ per unit of area in the state of reference. The symbolism clearly indicates the physical signification; the accented $_{X'}$ in the suffix indicates that the force *is* estimated on an area which *was* perpendicular to OX' in the unstrained state and was equal to the unit of area in that state. The unaccented X, to which $_{X'}$ is the suffix attached, indicates that the force is a component in the direction OX. The force of course only exists in the strained state, since the reference state is assumed as an unstrained state, that is, one in which the stress-constituents vanish. (See the remarks on this on page 418.)

It is clear from this (quite apart from the type of equations connecting $X_{X'}$, ... $Z_{Z'}$ with X_X, ... Z_Z which are indicated above) that X_X is quite distinct from $X_{X'}$; for X_X is the force across a face which *is* perpendicular to OX in the state of strain estimated on an area which is equal to the unit area in that state; it is however, like $X_{X'}$, a component in the direction OX. Similar differences can be drawn between the other components of stress in the two systems of coordinates. From this it can be perceived that because $Y_Z = Z_Y$ it is not of necessity true that $Y_{Z'} = Z_{Y'}$. It should be observed that these results do not depend on the fact that one may choose the axes OX, OY, OZ not to coincide with OX', OY', OZ'; for even if they were made to coincide the symbol X_X, for example, could not be made to do double service, on the one hand for a component parallel to OX of a force across an area which *was* unit area in size and *was* perpendicular to OX, and on the other hand across an area which *is* unit area in size and *is* perpendicular to OX. Thus the double naming of the axes is of service even when they are regarded as coincident. This is a justification for Gibbs' apparently pointless complication of procedure. Only if the state of strain is regarded as being little removed from the state of reference can we assume that an approximate equality may exist between $Y_{X'}$ and $X_{Y'}$, and so on, provided the two sets of axes are regarded as coincident.

At the risk of appearing to be prolix on this matter, the writer would like to point out that the equations (38) offer an alternative method of giving the correct physical signification to $X_{X'}$, etc. If we recall the arguments developed from equations (16) to (27) above, we will remember on looking at (27) that a unit area, which *was* in the state of reference perpendicular to OX' (so that for it $\alpha' = 1$, $\beta' = 0$, $\gamma' = 0$), is strained into an area whose projections on the planes perpendicular to OX, OY, OZ are A_{11}, A_{21}, A_{31}, with similar results for unit areas originally normal to OY' or OZ'. In other words, if unit area which was in the state of reference perpendicular to OX' is strained into an area of size K with direction cosines α, β, γ with reference to OX, OY, OZ, then

$$\begin{aligned} K\alpha &= A_{11}, \\ K\beta &= A_{21}, \\ K\gamma &= A_{31}. \end{aligned}$$

But by (28), the force across this surface in the state of strain in the direction OX has the value $\alpha X_X + \beta X_Y + \gamma X_Z$ per unit area, and so the actual force across the area K in the state of strain is

$$A_{11}X_X + A_{21}X_Y + A_{31}X_Z,$$

which by (38) is just $X_{X'}$, thus giving us the physical interpretation of $X_{X'}$ once more. In the same way we can demonstrate that $X_{Y'}$ is the force parallel to OX across an area in the state of strain, which in the state of reference was unit area in size and normal to OY' in orientation; and so on.

6. *Thermodynamics of a Strained Homogeneous Solid.* The treatment of heterogenous systems in the earlier parts of Gibbs' discussion of the subject is of course based on equation [12] which is a generalization from equation [11], the equation for a homogeneous body when uninfluenced by distortion of solid masses (among other physical changes). In the same way any treatment of heterogenous substances in which elastic effects

must be taken into account will require a knowledge of how a homogeneous substance when strained must be dealt with in thermodynamical reasoning. The equation which is to replace [11] is now easily derived in view of what has just been accomplished in the previous parts of this exposition. Thus in [11] ϵ and η are regarded as functions determined completely by the state of the body. For a homogeneous fluid, we can regard them as functions of its temperature and volume, or of its temperature and pressure, and their differentials are connected by the equation

$$d\epsilon = td\eta - pdv. \tag{39}$$

If we consider this as applying to the matter within a unit of volume, dv is actually the fraction of dilatation, essentially the one strain-function which plays any part in the case of a fluid, since the elongation in all directions is uniform and shears do not exist. For a strained solid ϵ and η are still functions of the state, and we can take as the variables the temperature and the strain-coefficients. There are nine of the latter, but we have seen that six quantities are sufficient. In equations (9) we have defined six such quantities $e_1, e_2, \ldots e_6$, and later in (23) and (24) we have seen that they are quantities which are entirely independent of the choice of the axes in the strained state, (of course, their particular values depend on what axes we choose for OX', OY', OZ', the axes to which the unstrained state is referred; in particular we can choose axes so that e_4, e_5, e_6 vanish—the principal axes of the strain which are not sheared but merely rotated). For our immediate purpose it is more convenient to take the quantities $f_1, \ldots f_6$ as our "thermodynamical variables," where $f_1 = e_1^{\frac{1}{2}} - 1, \ldots, \ldots$; $f_4 = e_4/(e_2e_3)^{\frac{1}{2}}, \ldots, \ldots$ As we know, f_1 then represents the fraction of elongation parallel to OX', etc., and f_4 represents the shear of lines parallel to OY', OZ', etc.

For a fluid body $-p\delta v$ represents the change of internal energy of strain (compression) when the (unit) volume experiences a dilatation whose fraction is δv. Similarly, when the strain-functions $f_1, \ldots f_6$ are altered, the energy of strain of unit volume of the strained material alters by $X_1\delta f_1 \ldots + X_6\delta f_6$.

Here we make a natural generalization and assume that for any change of state of a homogeneous solid

$$d\epsilon = t d\eta + X_1 df_1 \ldots + X_6 df_6. \tag{40}$$

Fully interpreted this means that we consider ϵ and η to be functions of t, f_1, ... f_6. Strictly we should write them $\epsilon(t, f_1, \ldots f_6)$ and $\eta(t, f_1, \ldots f_6)$. If the state of the solid alters to *another state of equilibrium* in which the variables change to $t + dt$, $f_1 + df_1$, ... $f_6 + df_6$, then equation (40) connects the various differentials.

It will help us if we briefly recall how from equation (39) we derive the equations which connect those thermal and mechanical properties of fluids which can be observed and measured by experimental methods. Thus

$$d\eta = \frac{c_v(t, v)}{t} dt + \frac{l_v(t, v)}{t} dv, \tag{41}$$

where c_v is the specific heat at constant volume, and l_v the so-called latent heat of change of volume at constant temperature. We are, at the moment, taking t and v as the variables and indicating this precisely by writing the symbols in brackets after each quantity to show that in each case we are considering the appropriate functional form which expresses that quantity in terms of these variables. This device will also indicate without any ambiguity what quantities are being regarded as constant when we write down any *partial* differential coefficient. From the equation

$$d\epsilon(t, v) = t d\eta(t, v) - p(t, v)dv,$$

we derive the differential equation of the Gibbs ψ function (free energy at constant volume), viz.,

$$d\psi(t, v) = -\eta(t, v)\, dt - p(t, v)dv, \tag{42}$$

where

$$\psi = \epsilon - t\eta.$$

Thus

$$\frac{\partial \eta(t, v)}{\partial v} = \frac{\partial p(t, v)}{\partial t}. \tag{43}$$

But by (41)

$$l_v = t\,\frac{\partial \eta(t, v)}{\partial v}.$$

Therefore

$$l_v = t\,\frac{\partial p(t, v)}{\partial t}, \tag{44}$$

the well known relation connecting the latent heat of change of volume at constant temperature with the temperature coefficient of pressure at constant volume. Also from (41) we derive

$$\begin{aligned}\frac{\partial c_v(t, v)}{\partial v} &= \frac{\partial}{\partial v}\left\{t\,\frac{\partial \eta(t, v)}{\partial t}\right\} \\ &= t\,\frac{\partial^2 \eta(t, v)}{\partial t \partial v}.\end{aligned}$$

But by (43)

$$\frac{\partial^2 \eta(t, v)}{\partial t \partial v} = \frac{\partial^2 p(t, v)}{\partial t^2}.$$

Hence

$$\frac{\partial c_v(t, v)}{\partial v} = t\,\frac{\partial^2 p(t, v)}{\partial t^2}, \tag{45}$$

which is another well-known relation.

If we choose we can take the temperature and pressure as the thermodynamical variables. We then write

$$d\eta(t, p) = \frac{c_p(t, p)}{t}\,dt + \frac{l_p(t, p)}{t}\,dp, \tag{46}$$

where c_p and l_p are the specific heat at constant pressure and the latent heat of change of pressure at constant temperature. Another differential equation which we require now is that for the ζ function of Gibbs (the "free energy at constant pressure")

$$d\zeta(t, p) = -\eta(t, p)dt + v(t, p)dp, \tag{47}$$

where

$$\zeta = \epsilon - t\eta + pv.$$

From this we derive

$$\frac{\partial \eta(t, p)}{\partial p} = -\frac{\partial v(t, p)}{\partial t}. \tag{48}$$

But by (46)

$$l_p = t\frac{\partial \eta(t, p)}{\partial p}.$$

Therefore

$$l_p = -t\frac{\partial v(t, p)}{\partial t}, \tag{49}$$

a well-known relation.

Also, from (46),

$$\frac{\partial c_p(t, p)}{\partial p} = t\frac{\partial^2 \eta(t, p)}{\partial t \partial p}.$$

But by (48)

$$\frac{\partial^2 \eta(t, p)}{\partial t \partial p} = -\frac{\partial^2 v(t, p)}{\partial t^2}.$$

Hence

$$\frac{\partial c_p(t, p)}{\partial p} = -\frac{\partial^2 v(t, p)}{\partial t^2}. \tag{50}$$

There remains one more well-known relation.

If an infinitesimal change takes place *at constant pressure,* the change of entropy is equal, by equation (41), to

$$\frac{1}{t}\left\{ c_v(t, v)dt + l_v(t, v)\,\frac{\partial v(t, p)}{\partial t}\,dt \right\}.$$

It is also, by (46), equal to

$$\frac{1}{t}\,c_p(t, p)dt.$$

Equating these two expressions we obtain the result

$$c_p(t, p) = c_v(t, v) + l_v(t, v)\,\frac{\partial v(t, p)}{\partial t},$$

and using (44) we arrive at

$$c_p - c_v = t\,\frac{\partial p(t, v)}{\partial t}\,\frac{\partial v(t, p)}{\partial t}. \tag{51}$$

In exactly the same manner we can derive the equations which connect the thermal and mechanical properties of a solid. For the sake of brevity we shall write $\epsilon(t, f)$ and $\eta(t, f)$ for $\epsilon(t, f_1, \ldots f_6)$ and $\eta(t, f_1, \ldots f_6)$; so that when we write, for example,

$$\frac{\partial \eta(t, f)}{\partial t} \qquad \text{or} \qquad \frac{\partial \eta(t, f)}{\partial f_r},$$

we mean the temperature variation of η at constant strain or the rate of variation of η with respect to f_r, the temperature and the five strain functions other than f_r being maintained constant. In analogy with (41) we write

$$d\eta(t, f) = \frac{c(t, f)}{t}\,dt + \sum \frac{l_r(t, f)}{t}\,df_r. \tag{52}$$

The summation extends over six terms; c is the specific heat at constant strain of the solid (per unit volume as measured in the state of strain), which means that the solid is prevented from changing volume *and shape.* The six quantities l_r are various latent heats of change of strain; in each case the temperature and five strain-quantities are unchanged. A well-known illustration can be given of the idea involved here. When one extends a piece of rubber suddenly, it rises in temperature. Thus if one wished to maintain the temperature constant one would have to extend slowly and take heat from the solid, which shows that the l_r coefficients for rubber are negative. The energy relation (40) is now written

$$d\epsilon(t, f) = td\eta(t, f) + \Sigma X_r(t, f)df_r, \tag{53}$$

and from it we derive the differential equation for Gibbs' ψ function, viz.,

$$d\psi(t, f) = -\eta(t, f)dt + \Sigma X_r(t, f)df_r, \tag{54}$$

where

$$\psi = \epsilon - t\eta.$$

From (54) we derive

$$\frac{\partial\eta(t, f)}{\partial f_r} = -\frac{\partial X_r(t, f)}{\partial t}. \tag{55}$$

But by (52)

$$l_r = t\frac{\partial\eta(t, f)}{\partial f_r}.$$

Therefore

$$l_r = -t\frac{\partial X_r(t, f)}{\partial t}. \tag{56}$$

There are of course six equations of the type (56), and they connect the heat required to maintain the temperature constant when the strains are altered with the variations of stress required to maintain the strains constant (i.e., to prevent expansion and change of shape) when the temperature alters. To continue, from (52) we derive

$$\frac{\partial c(t, f)}{\partial f_r} = t\frac{\partial^2\eta(t, f)}{\partial t\partial f_r}.$$

But by (55)

$$\frac{\partial^2\eta(t, f)}{\partial t\partial f_r} = -\frac{\partial^2 X_r(t, f)}{\partial t^2}.$$

Hence we obtain the six relations

$$\frac{\partial c(t, f)}{\partial f_r} = -t\frac{\partial^2 X_r(t, f)}{\partial t^2}. \tag{57}$$

It is, of course, open to us to choose as thermodynamic variables the temperature and the six components of stress. The energy and entropy are then expressed in full by the symbols $\epsilon(t, X_1, \ldots X_6)$ and $\eta(t, X_1, \ldots X_6)$ or briefly $\epsilon(t, X)$ and $\eta(t, X)$. The entropy equation then becomes

$$\eta(t, X) = \frac{C(t, X)}{t}\, dt + \sum \frac{L_r(t, X)}{t}\, dX_r, \tag{58}$$

where C is the specific heat at constant stress, i.e., under practically the usual conditions of measurement, where the external forces on the solid are unchanged. $L_1, \ldots L_6$ are six latent heats of change of stress, each one at constant temperature and with five of the stress-components unaltered.

The energy differential equation is once more adapted to the choice of variables by using Gibbs' ζ function, viz.,

$$\epsilon - t\eta - \Sigma X_r f_r.$$

Thus

$$d\zeta(t, X) = -\eta(t, X)dt - \Sigma f_r(t, X)dX_r. \tag{59}$$

From (59) we derive

$$\frac{\partial\eta(t, X)}{\partial X_r} = \frac{\partial f_r(t, X)}{\partial t}. \tag{60}$$

But by (58)

$$L_r = t\frac{\partial\eta(t, X)}{\partial X_r}.$$

Therefore

$$L_r = t\,\frac{\partial f_r(t, X)}{\partial t}, \tag{61}$$

giving us six equations connecting the heat required to maintain the temperature constant when the stresses are altered with the variations of strain which accompany changes of temperature when the stresses are maintained constant. In addition we derive from (58) the equation

$$\frac{\partial C(t, X)}{\partial X_r} = t\,\frac{\partial^2 \eta(t, X)}{\partial t \partial X_r},$$

and by (60)

$$\frac{\partial^2 \eta(t, X)}{\partial t \partial X_r} = \frac{\partial^2 f_r(t, X)}{\partial t^2}.$$

Hence we obtain the six relations

$$\frac{\partial C(t, X)}{\partial X_r} = t\,\frac{\partial^2 f_r(t, X)}{\partial t^2}. \tag{62}$$

A relation analogous to (51) can also be derived, which connects the difference of the two specific heats with the temperature coefficients of the strain-functions and the stress-constituents. Thus let an infinitesimal change take place *at constant stress*; the change of entropy can be expressed in two ways. For by (52) it is equal to

$$\frac{1}{t}\left\{ c(t, f)dt + \sum l_r(t, f)\,\frac{\partial f_r(t, X)}{\partial t}\,dt \right\},$$

and by (58) it is also equal to

$$\frac{1}{t}\,C(t, X)\,dt.$$

Equating these two expressions we obtain the result

$$C(t, X) = c(t, f) + \sum l_r(t, f)\,\frac{\partial f_r(t, X)}{\partial t},$$

and using (56) we reach, finally,

$$C - c = -t \sum \frac{\partial X_r(t, X)}{\partial t} \frac{\partial f_r(t, X)}{\partial t}. \tag{63}$$

Some further relations can be obtained from the differential equations for the entropy and various energy functions. Thus from (52) we see that

$$l_r(t, f) = t \frac{\partial \eta(t, f)}{\partial f_r},$$

$$l_s(t, f) = t \frac{\partial \eta(t, f)}{\partial f_s}.$$

Hence

$$\frac{\partial l_r(t, f)}{\partial f_s} = \frac{\partial l_s(t, f)}{\partial f_r}, \tag{64}$$

and there are fifteen such "reciprocal relations" between the latent heats and the strains.

Similarly from (54) we obtain fifteen reciprocal relations between the stresses and strains, viz.,

$$\frac{\partial X_r(t, f)}{\partial f_s} = \frac{\partial X_s(t, f)}{\partial f_r}. \tag{65}$$

By using equations (58) and (59) we can obtain two sets of reciprocal relations, one between the latent heats and stresses, one between the strains and stresses, viz,

$$\frac{\partial L_r(t, X)}{\partial X_s} = \frac{\partial L_s(t, X)}{\partial X_r} \tag{66}$$

and

$$\frac{\partial f_r(t, X)}{\partial X_s} = \frac{\partial f_s(t, X)}{\partial X_r}. \tag{67}$$

From the thermodynamic equations we can also give a more general signification to the elastic constants of a solid, which were introduced in equations (31) as purely mechanical conceptions. By means of equations (53) or (54) we can express the stress-constituents as functions of the temperature and the strains; thus

$$X_r = \frac{\partial\psi(t, f)}{\partial f_r}. \tag{68}$$

Now suppose the body experiences a small variation of strain *at constant temperature*; the variations in the stresses are given by the six equations

$$\delta X_r = c_{r1}\delta f_1 \ldots + c_{r6}\delta f_6, \tag{69}$$

where

$$\left.\begin{aligned} c_{rs} &= \frac{\partial X_r(t, f)}{\partial f_s} \\ &= \frac{\partial^2\psi(t, f)}{\partial f_r\, \partial f_s}. \end{aligned}\right\} \tag{70}$$

Equation (69) replaces (31). The elastic constants are of course functions of the temperature and the strains. If the ψ function is quadratic in the strains, the quantities c_{rs} are independent of the strains, and this leads to the generalized Hooke's law referred to earlier. In any case equation (70) shows that $c_{rs} = c_{sr}$ and that at the most there are only 21 elastic constants. For an isotropic material, we have as before essentially only two, the bulk modulus or elasticity of volume, defined as before, and the modulus of rigidity given by any one of the differential coefficients

$$\left.\begin{array}{lccc} & \dfrac{\partial X_4(t, f)}{\partial f_4}, & \dfrac{\partial X_5(t, f)}{\partial f_5}, & \dfrac{\partial X_6(t, f)}{\partial f_6}, \\ \text{or} & & & \\ & \dfrac{\partial^2\psi(t, f)}{\partial f_4^2}, & \dfrac{\partial^2\psi(t, f)}{\partial f_5^2}, & \dfrac{\partial^2\psi(t, f)}{\partial f_6^2}, \end{array}\right\} \tag{71}$$

which are equal for such a substance.

For those interested to pursue these matters further, a short chapter on the thermodynamics of strain will be found in Poynting & Thomsons' *Properties of Matter*. For a very full treatment consult Geiger and Scheel's *Handbuch der Physik*, Vol. VI, Chap. 2, pp. 47–60 (Springer, Berlin).

We have now completed this long exposition of elastic solid theory. It has been necessary to go into it in some detail, since without some modicum of knowledge concerning it, this section of Gibbs' treatment, brief as it is, would be utterly unintelligible. Indeed its very brevity renders the task more difficult; for although Gibbs, in his treatment of heterogeneous phases consisting of solids and fluids, does not employ in every detail the analysis of stress and strain in a solid usual in the texts of to-day, every now and then he interposes a short remark which would puzzle a reader unacquainted with that analysis. The very first page of the section is a case in point. Moreover, this analysis usually forms part of one of the more specialized courses in the physics or mathematics department of a university, and even students of physics, not aiming at a highly specialized degree in that subject, might well find their knowledge of stress and strain too rudimentary to follow Gibbs at this point.

We now take the section itself and give a commentary upon it page by page.

II. Commentary

7. Commentary on Pages 184–190. Derivation of the Four Equations Which Are Necessary and Sufficient for the Complete Equilibrium of the System. We have already in the preceding exposition dealt extensively with the introductory definitions and formulations of Gibbs, I, pp. 184–186. We would remind readers that in [354] the usual practice of to-day would replace a differential coefficient such as dx/dz' by $\partial x/\partial z'$, since it is implied that x, regarded as a function of x', y', z', is being differentiated *partially* with respect to z', with the condition that x' and y' do not change in value. Actually it will probably be more convenient if we keep the notation introduced above and refer to $\partial x/\partial x'$ as a_{11}, $\partial x/\partial y'$ as a_{12}, $\partial y/\partial x'$ as a_{21}, etc. If the strain is homogeneous these a_{rs} strain-coefficients are independent of the particular values of x', y', z'; they are constant throughout the solid body. In general, however, the strain may be heterogeneous, and in that event any a_{rs} is a function of x', y', z', and a_{rs} implies a functional form and is really a contraction for $a_{rs}(x', y', z')$.

Care should be exercised also to retain a clear idea of the meaning of the variational symbol δ. We have already used it in the exposition in the sense in which it is employed by Gibbs; thus $\delta(\partial x/\partial x')$ or, as we shall write it, δa_{11} refers to an infinitesimal variation of the strain-coefficient, *at a given point*, i.e., in a given physically small element surrounding the point which was originally at x', y', z'. The reader must guard himself carefully against the misconception that he is to think of a point neighboring to x', y', z', say $x' + \delta x'$, $y' + \delta y'$, $z' + \delta z'$, and to regard δa_{11} as short for

$$\frac{\partial a_{11}}{\partial x'}\,\delta x' + \frac{\partial a_{11}}{\partial y'}\,\delta y' + \frac{\partial a_{11}}{\partial z'}\,\delta z',$$

i.e., as the difference between the strain-coefficient at a point and at a neighboring point. Such a blunder would be fatal to any understanding of [355]. Indeed it was to avoid giving the reader any unconscious bias toward such an idea, that the writer, in referring in the exposition to a point near to x', y', z' employed the notation $x' + \xi'$, $y' + \eta'$, $z' + \zeta'$ and not $x' + \delta x'$, etc.

In the exposition we used ϵ and η as symbols for the energy and entropy of the amount of material which occupies the unit of volume in the state of strain from which an infinitesimal variation is made; there was no need for suffixes as there was no ambiguity involved at that point. It is, however, the general practice of Gibbs to refer the material to its state of reference when considering magnitudes of measured properties per unit length, area or volume. Hence his use of the suffix V' to bring that clearly before the reader's mind. Occasionally when he wishes to make a statement concerning magnitudes measured per unit of volume in the state of strain he employs the suffix V without the accent.

In the exposition we saw that

$$d\epsilon_V = t\,d\eta_V + \Sigma X_r df.$$

Now a unit of volume in the state of reference becomes the volume $v_{V'}$ in the state of strain. (See Gibbs, I, 188, line 27.) This quantity is, as we proved in the exposition, the determinant of the a_{rs} coefficients, which is denoted later in Gibbs' discussion by the symbol H. If we multiply the differential equation written above by $v_{V'}$ we obtain

$$d\epsilon_{V'} = td\eta_{V'} + H\,\Sigma X_r df_r.$$

Also, the f_r coefficients are defined in the exposition as certain functions of $e_1, \ldots e_6$; i.e., of $a_1, \ldots a_6$ which are in their turn functions of the nine coefficients a_{rs}, so that any differential df_r can be expressed as a sum of the differentials da_{rs}, such as

$$\phi_{11}da_{11} + \phi_{12}da_{12} \ldots + \phi_{33}da_{33},$$

where $\phi_{11}, \phi_{12}, \ldots \phi_{33}$ are functions of $a_{11}, a_{12}, \ldots a_{33}$. In this way we arrive at Gibbs' expression [355], where $X_{X'}, X_{Y'}, \ldots Z_{Z'}$ are functions of $X_X, \ldots Z_Z, a_{11}, \ldots a_{33}$. The actual functional forms we have already developed in the exposition and given the actual linear relations which connect Gibbs' stress-constituents with the usual stress-constituents.

On page 187 we have an expression for the variation of the energy *of the solid body* if an infinitesimal amount of material is added to it. Again we must carefully distinguish between the variational symbol δ and the differential symbol D, and interpret correctly the use of the accents. Thus an element of the surface of the body in the state of strain is represented by Ds. If by crystallization from a surrounding fluid, for example, the body increases in size, the surface is displaced normally outwards by an infinitesimal amount which we represent by δN. This might be regarded as having a constant value everywhere on the surface, giving a uniform thickness for the additional layer. But this is not so of necessity; δN in general is regarded as a function of the position of the center of the element Ds, a function obviously infinitesimally small in value. Indeed δN could be regarded as some ordinary function $\phi(x, y, z)$ of the coordinates of a point on the surface multiplied by an infinitesimal constant. A sign of integration, of course, refers to the differential Ds. For example $\int \delta N Ds$ is the increase in volume of the solid as it is when the deposition of matter takes place, viz., in the state of strain. (Note lines 4 and 5, where Gibbs expressly indicates this.) We could, however, conceive the solid to be brought back to the unstrained state after the deposition, the additional matter following the same change. In consequence the solid would be larger in its unstrained state than the original solid (before the increment) in the unstrained state by an amount $\int \delta N' Ds'$; where $\delta N'$ now represents the thickness of the additional layer in the unstrained state and Ds' the size of the element of area which is Ds in the strained state. Since $\epsilon_{V'}$ refers to the quotient of the energy of strain of a small portion of the *strained* matter by its volume in the unstrained state, the expression $\int \epsilon_{V'} \delta N' Ds'$ is justified. (It could, of course, be just as well represented by $\int \epsilon_V \delta N Ds$, but the former expression is the more convenient for Gibbs' argument.) In cases where the solid has in part dissolved, δN and $\delta N'$ would be negative in value. Thus we arrive at expression [357] for the variation of the intrinsic energy of the solid.

We are not however concerned with this energy alone, nor with the entropy and mass of the solid alone. The system is heterogeneous and involves fluid phases also, and so we are led to the considerations dealt with in the remainder of page 187. Again the *form* of [358] may puzzle readers not acquainted with the methods of the calculus of variations, although the *content* or meaning of it should not be very much in doubt. The passage of matter and heat to (or from) the solid from (or to) the liquid will change the entropy $D\eta$ and the volume Dv of a given elementary mass of the fluid by amounts $\delta D\eta$ and δDv; and in addition will alter the masses of the constituents Dm_1, Dm_2, etc., composing it. The condition laid down towards the end of page 187, which obviates the necessity of dealing with the internal equilibrium of the fluid itself, involves as a natural result the simplification that the integrations throughout the narrow layers of fluid between rigid envelop and solid are free from any troubles concerning original and present states, and do not require the use of accents to avoid ambiguity. Expression [359] embodies the fact that the potential energy of an element of matter m, raised through a height δz, acquires potential energy of an amount $mg\delta z$.

The method of dealing with the variational equation [360] is essentially the same as that of dealing with the variational equation [15] in the early pages of Gibbs' discussion, although the presence of integral signs and merely *formal* differences of appearance between [15] and [360] may mask the identity of the methods. It would have been quite legitimate to write in [15] $\int\int\int t'\delta\eta'_{V'}dx'dy'dz'$ for $t'\delta\eta'$, the integration being throughout the phase indicated by one accent, and so on; but it was unnecessary, as the conditions were uniform throughout any given phase in equilibrium. But for a solid the strain may be heterogeneous, and so $\eta_{V'}$ might well change in value from point to point of the solid body with the changing values of $a_{11}, a_{12}, \ldots a_{33}$. Hence the necessity for the integral. Also if the strain were homogeneous we could write the second term in [360] as $V'\Sigma\Sigma' X_{X'}\delta a_{11}$, V' being the volume (unstrained) of the solid; but in general this is not possible. Reflection on this and similar considerations for the remaining terms will remove any difficulty in understanding raised by pure differences of form. Following this hint we see that [361], [362] and [363] are the additional equations arising from constancy of total entropy, from constancy of the total volume of the system within the envelop, and from constancy of total mass of an independent constituent of the system; they are entirely analogous to equations [16], [17] and [18] respectively. Condition [361] is straightforward. In [362] we consider any element of the fluid Dv in the form of a thin disc lying between an element of surface Ds of the solid and a similar element of the rigid envelop. First of all the variation of the strain in the solid involves displacements δx, δy, δz of the point x, y, z, the center of Ds; thus Ds is displaced normally towards the envelop by $\alpha\delta x + \beta\delta y + \gamma\delta z$. This reduces the volume Dv by an amount $(\alpha\delta x + \beta\delta y + \gamma\delta z)Ds$. In addition the accretion of new matter reduces it also by δNDs or $v_{V'}\delta N'Ds'$ as we saw above. These two causes therefore bring about a change δDv in Dv which is given by [362]. Equation [363] offers no difficulty. The subsequent reasoning leading to equation [369] is based on an application of Lagrange's method of multipliers, referred to and used earlier in Gibbs' discussion.

(See Gibbs, I, 71–74.) The object of the method is to eliminate certain of the variations from the condition of equilibrium so as to leave in it only those variations which are independent of each other and are therefore completely arbitrary in their relative values. Those variations which can be regarded as arbitrary are the displacements of the points in the solid and on the surface arising from the arbitrary variation of strain in the solid, and also the thickness of the layer of material deposited on or dissolved off the solid. The object is partly attained by the time we reach equation [367] and the steps are fairly obvious; but in addition to δx, δy, δz and $\delta N'$ we have also the nine variations δa_{11}, δa_{12}, ... δa_{33}. But as we have seen these are not independent of each other since straining only depends on six functions of a_{11}, a_{12}, ... a_{33}. The step from [367] to [369] actually eliminates them all and replaces them by variations δx, δy, δz for points in the solid and on its surface. Gibbs is very brief at this point, and to elucidate the step made in [368] we shall have to make a short digression. The point $P'(x', y', z')$ in the reference state is displaced to $P(x, y, z)$ during the strain a_{11}, a_{12}, ... a_{33}. The additional strain δa_{11}, δa_{12}, ... δa_{33} displaces it still further to $P_\delta(x + \delta x, y + \delta y, z + \delta z)$. Hence the variation in the value of a_{11}, i.e., δa_{11} or $\delta(\partial x/\partial x')$, is equal to

$$\frac{\partial(x + \delta x)}{\partial x'} - \frac{\partial x}{\partial x'}.$$

Thus

$$\delta\left(\frac{\partial x}{\partial x'}\right) = \frac{\partial}{\partial x'}\,\delta x.$$

Similarly

$$\delta\left(\frac{\partial x}{\partial y'}\right) = \frac{\partial}{\partial y'}\,\delta x.$$

(Note that x, y, z are definite functions of x', y', z' and $x + \delta x$, $y + \delta y$, $z + \delta z$ are also definite functions of x', y', z' slightly different in value from the former; thus δx, δy, δz are also definite functions, small in value, of x', y', z'.) On this account

$$X_{X'}\,\delta a_{11} = X_{X'}\,\delta\left(\frac{\partial x}{\partial x'}\right)$$

$$= X_{X'}\,\frac{\partial}{\partial x'}\,\delta x,$$

which on integrating by parts is equal to

$$\frac{\partial}{\partial x'}\,(X_{X'}\,\delta x) - \frac{\partial X_{X'}}{\partial x'}\,\delta x.$$

Hence

$$\int\!\!\int\!\!\int X_{X'}\,\delta a_{11}\,dx'dy'dz' = \int\!\!\int\!\!\int \frac{\partial}{\partial x'}\,(X_{X'}\,\delta x)\,dx'dy'dz'$$
$$- \int\!\!\int\!\!\int \frac{\partial X_{X'}}{\partial x'}\,\delta x\,dx'dy'dz'.$$

The first integral on the right hand side, which is an integral throughout the volume of the solid, can be transformed by Green's theorem into an integral over its surface, viz.,

$$\int \alpha' X_{X'}\delta x Ds',$$

and in consequence we obtain the result [368]. (Will the reader accept the truth of this transformation for the moment so as not to interrupt the argument? We shall return in a moment to Green's theorem for the sake of those unacquainted with it.) In a similar manner

$$X_{Y'}\,\delta a_{12} = X_{Y'}\,\delta\left(\frac{\partial x}{\partial y'}\right)$$

$$= X_{Y'}\,\frac{\partial}{\partial y'}\,\delta x$$

$$= \frac{\partial}{\partial y'}\,(X_{Y'}\,\delta x) - \frac{\partial X_{Y'}}{\partial y'}\,\delta x,$$

and therefore

$$\iiint X_{Y'}\,\delta a_{12}\,dx'dy'dz' = \iiint \frac{\partial}{\partial y'}(X_{Y'}\,\delta x)\,dx'dy'dz'$$
$$-\iiint \frac{\partial X_{Y'}}{\partial y'}\,\delta x\,dx'dy'dz'$$
$$= \int \beta'(X_{Y'}\,\delta x)\,Ds' - \iiint \frac{\partial X_{Y'}}{\partial y'}\,\delta x\,dx'dy'dz',$$

and so on. When we make the substitutions in the first integral of [367] justified by these transformations, we convert equation [367] into the form [369]. It might be as well to write the first integral in [369] in full for the sake of clarity; it is

$$-\iiint\left\{\left(\frac{\partial X_{X'}}{\partial x'}+\frac{\partial X_{Y'}}{\partial y'}+\frac{\partial X_{Z'}}{\partial z'}\right)\delta x\right.$$
$$+\left(\frac{\partial Y_{X'}}{\partial x'}+\frac{\partial Y_{Y'}}{\partial y'}+\frac{\partial Y_{Z'}}{\partial z'}\right)\delta y$$
$$\left.+\left(\frac{\partial Z_{X'}}{\partial x'}+\frac{\partial Z_{Y'}}{\partial y'}+\frac{\partial Z_{Z'}}{\partial z'}\right)\delta z\right\}dx'dy'dz'$$

where of course δx, δy, δz are to be regarded as functions of x', y', z', infinitesimal in value. Similarly the third integral written in full is

$$\int\{\ (\alpha' X_{X'}+\beta' X_{Y'}+\gamma' X_{Z'})\delta x$$
$$+(\alpha' Y_{X'}+\beta' Y_{Y'}+\gamma' Y_{Z'})\delta y$$
$$+(\alpha' Z_{X'}+\beta' Z_{Y'}+\gamma' Z_{Z'})\delta z\ \}Ds'.$$

We shall neglect for the moment the point raised at the bottom of page 189 concerning surfaces of discontinuity, returning to it when we give a proof of Green's theorem, and proceed with the general line of development. Taking the result [369] we shall rearrange it so as to collect all the terms involving δx, all those involving δy, all those involving δz and all those involving $\delta N'$. It is then written in the form

$$
\begin{aligned}
-\iiint\Big\{&\left(\frac{\partial X_{X'}}{\partial x'}+\frac{\partial X_{Y'}}{\partial y'}+\frac{\partial X_{Z'}}{\partial z'}\right)\delta x\\
&+\left(\frac{\partial Y_{X'}}{\partial x'}+\frac{\partial Y_{Y'}}{\partial y'}+\frac{\partial Y_{Z'}}{\partial z'}\right)\delta y\\
&+\left(\frac{\partial Z_{X'}}{\partial x'}+\frac{\partial Z_{Y'}}{\partial y'}+\frac{\partial Z_{Z'}}{\partial z'}-g\Gamma'\right)\delta z\Big\}\,dx'dy'dz'\\
+\int\Big\{&\left[\,(\alpha' X_{X'}+\beta' X_{Y'}+\gamma' X_{Z'})+\alpha p\,\frac{Ds}{Ds'}\right]\delta x\\
&+\left[\,(\alpha' Y_{X'}+\beta' Y_{Y'}+\gamma' Y_{Z'})+\beta p\,\frac{Ds}{Ds'}\right]\delta y\\
&+\left[\,(\alpha' Z_{X'}+\beta' Z_{Y'}+\gamma' Z_{Z'})+\gamma p\,\frac{Ds}{Ds'}\right]\delta z\Big\}\,Ds'\\
+\int&\left[\epsilon_{V'}-t\eta_{V'}+pv_{V'}-\sum(\mu_1\Gamma_1)\right]\delta N'\,Ds'\geqq 0.
\end{aligned}
$$

This is equation [369] written in full.

Since, in the volume integrals, δx, δy, δz are arbitrary variations, the expressions multiplying them must be zero at all points of the solid in order that [369] may be true for any relative values of δx, δy, δz. Thus we arrive at equations [374]. In the second integral of our rewritten [369] the expressions multiplying δx, δy, δz respectively must also be zero at all points of the surface for the same reason. Thus we arrive at equations [381]. There remains only the third integral in the rewritten [369]. If $\delta N'$ is quite arbitrary, i.e., if crystallization on the solid and solution from it are both possible we must accept the truth of [383]; but if the values of $\delta N'$ can only be chosen arbitrarily from infinitesimal negative numbers, i.e., if solution only is possible, we justify only the wider conclusion [384].

At the bottom of page 190, Gibbs makes a passing reference to the stress-constituents X_X, X_Y, ... Z_Z i.e., the constituents measured across faces perpendicular to the same axes as those which indicate the directions of the thrusts or pulls involved in the definitions of the constituents. His proof of the equality of X_Y to Y_X, Y_Z to Z_Y, Z_X to X_Z is one of those succinct, sweeping statements which he makes from time to time with complete justification, but with a whole array of intermediate steps in the reasoning omitted, to the bewilderment of the reader not so well versed in analytical processes. It was in view of the awkward situation at this point that we have in our discussion introduced and defined X_X, X_Y, ... Z_Z first, treating them in a manner which will have been familiar to any reader acquainted with modern texts on elasticity, and have already proved the equality of X_Y to Y_X, etc. Later, it will be recalled, we introduced Gibbs' more general stress-constituents $X_{X'}$, $X_{Y'}$, ... $Z_{Z'}$ and gave some care to their precise definition and to the equations (38) which connect them with X_X, X_Y, ... Z_Z. It will be apparent from these equations that in general $X_{Y'}$ is not equal to $Y_{X'}$, for example. Let us, however, make the two sets of axes coincide so that a_{11} becomes e_{11}, etc., and A_{rs}, the first minor of a_{rs} in the determinant $|a|$ becomes E_{rs}, the first minor of e_{rs} in the determinant $|e|$. Equations (38) will be replaced by equations in which E_{rs} is substituted for A_{rs}. Even so, as we pointed out earlier, $X_{X'}$ does not become identical with X_X, etc., unless the difference between the state of reference and the state of strain is so little that a rectangular parallelopiped in the one is but little distorted from that shape in the other. To elaborate this latter point a little more, it will be observed that in such a case the determinant

$$\begin{vmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{vmatrix}$$

approximates to the form

$$\begin{vmatrix} 1 & e_{12} & e_{13} \\ -e_{12} & 1 & e_{23} \\ -e_{13} & -e_{23} & 1 \end{vmatrix},$$

for e_{11}, e_{22}, e_{33} are little different from unity, and $e_{23} + e_{32}$, etc., from zero. It appears that in such case E_{11} approximates to unity since e_{23} is small and $1 + e_{23}^2$ differs but little from unity. Similar statements are true of E_{22} and E_{33}, while E_{23}, E_{32}, etc., all approximate to zero for similar reasons. On examining the modified equations (38) it will appear that in the event of such coincidences $X_{X'}$ approaches to X_X, $X_{Y'}$ to X_Y, $X_{Z'}$ to X_Z. We thus illustrate in another manner Gibbs' conception of gradually bringing not only axes of reference but the two states into coincidence. But it will be realized on a little thought that even if we have the states approximating to coincidence, but not the axes, the considerations just raised do not hold; for then a_{11}, a_{12}, ... a_{33} involve not only the actual elongations and shears but also the direction cosines of the axes OX, OY, OZ with reference to OX', OY', OZ' which change with any reorientation of the former relative to the latter. In consequence a_{11}, a_{12}, ... a_{33} do not approximate to unity in general even for slightly separated states, and A_{11}, A_{12}, ... A_{33} do not tend to the values which are the limits of E_{11}, E_{12}, ... E_{33}.

Gibbs' own proof may now be clearer to the reader. From [355]

$$X_{Y'} = \frac{\partial \epsilon_{V'}}{\partial a_{12}} \quad \text{and} \quad Y_{X'} = \frac{\partial \epsilon_{V'}}{\partial a_{21}}.$$

Under the conditions of coincidence assumed a_{12} approaches e_{12} and a_{21} approaches e_{21} in value. Hence the limit of $X_{Y'}$ is $\partial \epsilon_V/\partial e_{12}$ and that of $Y_{X'}$ is $\partial \epsilon_V/\partial e_{21}$ since under these circumstances $\epsilon_{V'}$ approaches ϵ_V. Now actually ϵ_V is a function of f_6, and f_6 becomes in the limit $e_{12} + e_{21}$. Since therefore in the limit

$$\frac{\partial \epsilon_V}{\partial e_{12}} = \frac{\partial \epsilon_V}{\partial f_6} \cdot \frac{\partial f_6}{\partial e_{12}} = \frac{\partial \epsilon_V}{\partial f_6}$$

and

$$\frac{\partial \epsilon_V}{\partial e_{21}} = \frac{\partial \epsilon_V}{\partial f_6} \cdot \frac{\partial f_6}{\partial e_{21}} = \frac{\partial \epsilon_V}{\partial f_6},$$

it follows that X_Y which is the limit of $X_{Y'}$ is equal to Y_X which is the limit of $Y_{X'}$. The reference in Gibbs to the difference being equivalent to a rotation simply recalls the fact that in the analysis of strain the e_{12} and e_{21} coefficients involved the strain through their sum and a rotation around the axis OZ through their difference. (See equations (7) of this article.)

The reader may at this point feel a little mystified about making the states of reference and of strain coincide; for in such case he may well ask, how can one have stresses at all. If he will refer to the top of page 185, and read over the remarks on this point by Gibbs, he will feel once more that they are too brief to be very illuminating. The essential point is this. We are after all not treating the state of strain itself and its relation to a state of reference which is *physically* an unstrained state; we are treating other states of strain obtained by slight deformations from the state of strain in question, involving variations of a_{11}, etc.; and for that purpose it does not matter what particular state, strained or not, we take for a state of reference. The position is similar to the treatment of the geometry of a surface. There we are considering the relations of points on a given geometrical locus to some other geometrically relevant point (e.g., spherical surface to center, cone to apex, etc.) and it does not matter theoretically what particular set of axes we set up for assigning coordinates to the points in question. We choose in each case a set which is practically the most convenient. To give as wide a theoretical basis as possible to his analysis, Gibbs does not confine himself to any particular set of axes or any particular state of reference; but he does at this point make a passing reference to those axes and states which in practice are the most convenient by reason of the simplifications which they make possible, and to which we confined ourselves, for that reason, at the outset of our discussion of elastic solid theory.

Before we go on to comment on pages 191–207 in which Gibbs goes into certain details connected with equations [374], [381] and [383], it will be as well to dispose of the question of discontinuity referred to at the bottom of page 189. We have already mentioned that in deriving [369] from [367] Green's theorem is used. This theorem states that, if $\phi(x', y', z')$ is a function which is continuous, one-valued and finite throughout a region of space bounded by a surface s', then the three following relations are true

$$\iiint \frac{\partial\phi}{\partial x'}\,dx'\,dy'\,dz' = \int \alpha'\phi\,Ds',$$

$$\iiint \frac{\partial\phi}{\partial y'}\,dx'\,dy'\,dz' = \int \beta'\phi\,Ds',$$

$$\iiint \frac{\partial\phi}{\partial z'}\,dx'\,dy'\,dz' = \int \gamma'\phi\,Ds',$$

where the volume integrations are to be taken throughout the region bounded by s' and the surface integrals over s'. Figure 7 illustrates the proof of the first equation. The region is divided by up into elementary columns parallel to OX', whose sections by planes parallel to $OY'Z'$ are elementary rectangles, bounded by sides parallel to OY' and OZ'. Let us integrate $(\partial\phi/\partial x')dx'dy'dz'$ throughout that part of the region contained in one of the columns which intersects the surface in two elements of area $Ds_A{}'$ and $Ds_B{}'$ at the points A and B; the result is in the limit equal to the product of the definite integral $\int_B^A (\partial\phi/\partial x')dx'$ by the sectional area of the column. Now the definite integral is equal to $\phi_A - \phi_B$, where ϕ_A and ϕ_B are the values of $\phi(x', y', z')$

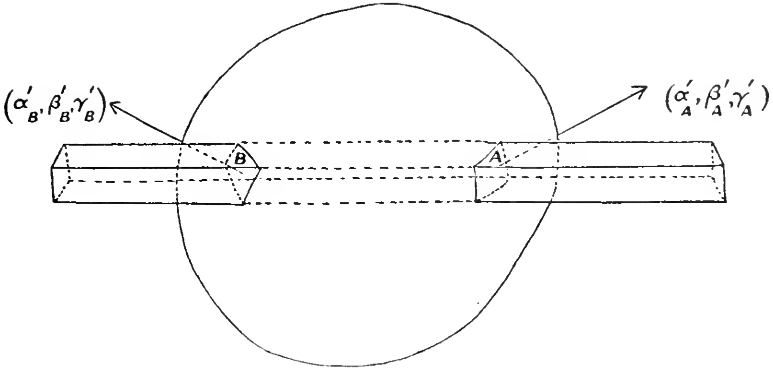
$(\alpha'_B, \beta'_B, \gamma'_B)$
$(\alpha'_A, \beta'_A, \gamma'_A)$
B
A

FIG. 7

at the points A and B respectively. Also if α_A', β_A', γ_A' and α_B', β_B', γ_B' are the direction cosines of the outward normals to s' at A and B, respectively, then $\alpha_A'Ds_A'$ and $-\alpha_B'Ds_B'$ are each equal to the sectional area, since the sectional area is equal to the projection of either of these sections by the surface on the plane $OY'Z'$, and α' is the cosine of the angle between the normal to an element of the surface and OX', which is normal to $OY'Z'$. (The figure shows that the minus sign is necessary in one of the results, since in one case the normal directed outwards will make an obtuse angle with OX'.) Hence the result of integrating $(\partial\phi/\partial x')dx'dy'dz'$ throughout the part of the region within this column is equal to

$$\alpha_A'\phi_A Ds_A' + \alpha_B'\phi_B Ds_B'.$$

Adding similar results for all such columns and passing to the limit we obtain the first of the relations given above. The remaining two are obtained by employing columns parallel to OY' and to OZ'. In the derivation of [368] by means of this theorem the function ϕ is $X_{X'}\delta x$.

Suppose, however, that in the above proof $\phi(x', y', z')$ is discontinuous at a certain surface s'' which divides the region of integration into two parts. If AB (Fig. 8) intersects this surface s'' in C then as we approach C in passing along BA from B the function $\phi(x', y', z')$ reaches as a limit a value ϕ_{C1} which differs finitely from the limit ϕ_{C2} which is reached as we approach C along AB from A. In applying Green's theorem now we must apply it separately to the two regions and integrate $(\partial\phi/\partial x')\, dx'\, dy'\, dz'$ first along a column stretching from B to C taking ϕ_{C1} as the value at C, and then along the column from C to A taking ϕ_{C2} as the value at C. In this way we arrive at the result

$$\iiint \frac{\partial\phi}{\partial x'}\, dx'\, dy'\, dz' \text{ (throughout the column)}$$

$$= \alpha_B'\, \phi_B\, Ds_B' + \alpha_{C1}''\, \phi_{C1}\, Ds_C'' + \alpha_{C2}''\, \phi_{C2}\, Ds_C'' + \alpha_A'\, \phi_A\, Ds_A',$$

where the direction cosines with the suffix 1 are for the normal to Ds_C'' directed outwards from the first part into which the region is divided by s'', and those affected by the suffix 2 for the normal directed outwards from the second part. (Of course $\alpha_1'' = -\alpha_2''$, $\beta_1'' = -\beta_2''$, $\gamma_1'' = -\gamma_2''$.) On adding results for all the columns we obtain the result

$$\int\int\int \frac{\partial \phi}{\partial x'}\, dx'\, dy'\, dz' = \int \alpha'\phi\, Ds' + \int (\alpha_1''\,\phi_1 + \alpha_2''\,\phi_2)\, Ds'',$$

and two similar results can be derived by using columns parallel to the axes OY' and OZ'.

If considerations such as these are given their due weight when discontinuities in the nature and state of the solid exist, it follows that in [369] a further term must be included on the left hand side, viz., the integral over such a surface of discontinuity, represented by

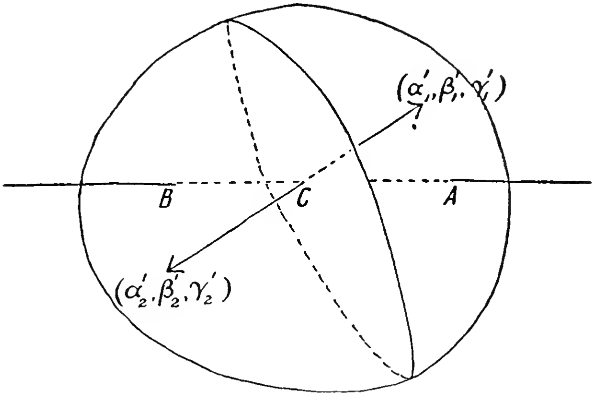
$(\alpha_1', \beta_1', \gamma_1')$
B
C
A
$(\alpha_2', \beta_2', \gamma_2')$

FIG. 8

$$\int \Sigma\Sigma' \{\alpha_1''(X_{x'}\delta x)_1 + \alpha_2''(X_{x'}\delta x)_2\} Ds'',$$

where δx, δy, δz, whether in the terms affected by the suffix 1 or in those affected by 2, refer of course to the same variation, viz., the variation in position of a point on the surface of discontinuity arising from an arbitrary change of strain; since this is just as arbitrary as the variation of any other point in the interior of the solid or on the surface bounding the solid, we must conclude that the three factors in the integrand multiplying δx, δy, δz are severally zero, and so we arrive at [378]. (The doubly accented direction-cosine symbols used in the argument for the sake of distinction between s' and s'' are, of course, not required any longer.) The expression referred to in [379], and the two similar expressions are of course the expressions in (29a) of this article, except that the former are the components of the stress-action at a surface on an area which was unit size in the state of reference, the latter on one which is unit size in the state of strain. The interpretation then put on [378] is obviously necessary for the equilibrium of an internal thin layer of the solid, bounded by two surfaces parallel and near to the surface of discontinuity, one in one part of the solid and one in the other.

8. Commentary on Pages 191–197. Discussion of the Four Equations of Equilibrium. Let us now resume the commentary on details in pages 191–197. The equations [377] are a particular case of (29) of this article in which the components F_x, F_y of the force per unit volume are zero and $F_z = -g\Gamma$. (Remember that OZ is directed upwards so that gravity is in the negative direction of OZ.) The meaning of the remarks which immediately follow concerning [375] and [376] may perhaps not be obvious to all readers at first sight. When we proved these equations in this exposition, we assumed that the solid was in equilibrium, but strictly this assumption was unnecessary. For if we refer once more to the proof leading to equation (30) and do not assume equilibrium, we must put the couple on the element of volume arising from the stresses of the surrounding matter and from the body forces on it equal, not to zero, but to the sum of the moments of the mass-acceleration products of the various particles of the element; i.e., to the product of the moment of inertia of the element and the angular acceleration. Now, without going into too much detail, this moment-sum, like the moment of the body forces, involves terms which have as a factor the product $\xi\eta\zeta$ and a length of the same order of magnitude as ξ, η or ζ. In consequence it is evanescent, just as is the moment of the body forces, in comparison with the moment of the stress-actions, and the same result follows as before. In consequence [375] and [376] are true in conditions other than those of equilibrium; they express in fact, as Gibbs says, "necessary relations,"—necessary, that is, in the sense that otherwise there would be involved a contradiction with the laws of dynamics in situations more general than those considered in the text.

The equations [381] should be compared with (29a) of this article, in which the expression $(\alpha X_X + \beta X_Y + \gamma X_Z)Ds$ is the stress-action across Ds in the direction OX of surface matter on interior matter, and $-\alpha p Ds$ is $F_x Ds$, the x-component of the external force on Ds. The difference here is purely formal, since $(\alpha' X_{X'} + \beta' X_{Y'} + \gamma' X_{Z'})Ds'$ is still the stress-action of surface matter on internal matter across the same element of area which *was* Ds' in the state of reference. The transformation of the equations to the form [382], which involves throughout the direction cosines α', β', γ' of the element in its state of reference, can be obtained at once without going through the argument in Gibbs, I, 192, 193; for we have already considered that argument in somewhat greater detail when proving equations (18) and (27). The notation we used in our discussion allows us to write equations [382] more fully, thus,

$$\alpha' X_{X'} + \beta' X_{Y'} + \gamma' X_{Z'} + p\{\alpha' A_{11} + \beta' A_{12} + \gamma' A_{13}\} = 0,$$

and two similar equations, since by (27)

$$\alpha \frac{Ds}{Ds'} \left(= \frac{K\alpha}{K'} \right) = \alpha' A_{11} + \beta' A_{12} + \gamma' A_{13}$$

and A_{11} is the second minor of a_{11} in the determinant $|a|$, i.e.,

$$\begin{aligned} A_{11} &= a_{22}a_{33} - a_{23}a_{32}, \\ &= \frac{\partial y}{\partial y'}\frac{\partial z}{\partial z'} - \frac{\partial z}{\partial y'}\frac{\partial y}{\partial z'}, \end{aligned}$$

and so on.

We pass on to the arguments based on equation [386] or [387]. The symbols p and μ_1 refer of course to the surrounding fluid (μ_1 being the potential of the solid substance in the liquid); ϵ_{V}, η_{V} and Γ, to the solid. The subsequent discussion is limited to the case of a solid body which is not only homogeneous in nature, but also *homogeneous in its state of strain.* The first point considered by Gibbs is concerned with the conditions under which this latter proviso is compatible with a uniform normal pressure over any finite portion of the surface. (The effect of gravity, the only body force considered in the general discussion preceding, is disregarded as negligible in producing heterogeneity of strain or variation in the value of pressure at different points of the surface.) This leads at once to Gibbs' discussion concerning the three principal axes of stress on pages 194 and 195. We need not comment on this, as we have already proved the necessary propositions in our exposition, starting from an expression similar to [389]. Gibbs' proof is an analytical one based on the methods of the calculus as applied to questions of maximum-minimum values of functions of several variables, and will be easily followed by those acquainted with these methods, whereas the method we have used, being based on the elementary geometrical properties of the stress-quadric will probably be intuitively perceived by those not so well versed in mathematical analysis. Actually, if we revert for a moment to the form of equations [382] which we have written above, the conclusions arrived at in the paragraph which includes the equations [393], [394], [395] can be obtained in a very direct and suggestive manner. Equations [382] in our form can be written thus:

$$\left.\begin{aligned}
&(X_{X'} + A_{11}p)\alpha' + (X_{Y'} + A_{12}p)\beta' \\
&\qquad + (X_{Z'} + A_{13}p)\gamma' = 0, \\
&(Y_{X'} + A_{21}p)\alpha' + (Y_{Y'} + A_{22}p)\beta' \\
&\qquad + (Y_{Z'} + A_{23}p)\gamma' = 0, \\
&(Z_{X'} + A_{31}p)\alpha' + (Z_{Y'} + A_{32}p)\beta' \\
&\qquad + (Z_{Z'} + A_{33}p)\gamma' = 0.
\end{aligned}\right\} \qquad [382a]$$

If the solid is in a given homogeneous state of strain, $X_{X'}, \ldots Z_{Z'}$,

$a_{11}, \ldots a_{33}$ are all constant and given in value throughout the solid. The same is true of the first minors $A_{11}, \ldots A_{33}$. In consequence [382a] combined with

$$\alpha'^2 + \beta'^2 + \gamma'^2 = 1$$

form a system of four equations to determine four "unknowns" α', β', γ', p, which will thus yield not only definite values of the fluid pressure, but also definite orientations of the solid surface compatible with this assigned state of strain. To see how many definite values and orientations are involved we consider [382a] carefully. Suppose that a definite value is assigned to p; this would give us three simultaneous equations to determine the values of the unknown α', β', γ', at least apparently. In reality, however, we should have *three* equations to determine *two* unknowns, viz., α'/γ' and β'/γ'. In short we have one equation too many; values of α'/γ' and β'/γ' which would satisfy the first two would not necessarily satisfy the third, unless a special relation existed between the nine coefficients. The relation embodies the fact that the determinant of the nine coefficients is zero, i.e.,

$$\begin{vmatrix} X_{X'} + A_{11}p & X_{Y'} + A_{12}p & X_{Z'} + A_{13}p \\ Y_{X'} + A_{21}p & Y_{Y'} + A_{22}p & Y_{Z'} + A_{23}p \\ Z_{X'} + A_{31}p & Z_{Y'} + A_{32}p & Z_{Z'} + A_{33}p \end{vmatrix} = 0.$$

Without actually multiplying this out, the reader will realize that the left-hand side is an expression involving p, p^2 and p^3. The equation is a cubic in p. Hence there are only *three* values of p which are compatible with the state of strain. They are the roots p_1, p_2, p_3 of this equation. If we insert one of these values, say p_1, into the first two of [382a] we can solve for the ratios α'/γ', β'/γ', and combining these with $\alpha'^2 + \beta'^2 + \gamma'^2 = 1$, we obtain values of α', β', γ', say α_1', β_1', γ_1'. Actually, as is obvious, $-\alpha_1'$, $-\beta_1'$, $-\gamma_1'$ will also satisfy the equations. (Not of course $-\alpha_1'$, β_1', γ_1' nor any triad with an arrangement of signs other than the two mentioned; for these would give ratios not satisfying [382a].) Inserting p_2 and p_3 we find that once more only a pair of orientations, given by α_2', β_2', γ_2'; $-\alpha_2'$, $-\beta_2'$, $-\gamma_2'$ and α_3', β_3', γ_3'; $-\alpha_3'$, $-\beta_3'$, $-\gamma_3'$, are compatible with these pressures respectively and the given state of strain. Furthermore, it can be proved from the equations that

$$\alpha_1'\alpha_2' + \beta_1'\beta_2' + \gamma_1'\gamma_2' = 0,$$
$$\alpha_2'\alpha_3' + \beta_2'\beta_3' + \gamma_2'\gamma_3' = 0,$$
$$\alpha_3'\alpha_1' + \beta_3'\beta_1' + \gamma_3'\gamma_1' = 0,$$

showing that the three directions are normal to each other; but the proof would lead us too far into the theory of such determinantal equations. Indeed, as doubtless many readers know, the analysis is quite similar to that employed in analytical geometry when determining the directions of the three principal axes of a quadric surface, and in fact Gibbs derives the result by a direct appeal to the existence of the three principal axes of stress which will, of course, have *the same directions at all points of the solid* if the strain is homogeneous. These directions are in fact the directions α_1', β_1', γ_1'; α_2', β_2', γ_2' and α_3', β_3', γ_3'; and p_1, p_2, p_3 are respectively $-X_X$, $-Y_Y$, $-Z_Z$ if the analysis of the stress-constituents has been referred to these principal axes as the axes of reference in the state of strain. (X_Y, Y_Z, Z_X, etc. are of course each zero in such case. In order to avoid confusion we have thus far had to use suffixed symbols for the three pressures instead of accented symbols; for the use of accented symbols to indicate measurements in the state of reference makes it awkward to use them for any other purpose, such as distinguishing three different values of a quantity. However, as the subsequent treatment will not require the use of direction-cosine symbols, we shall revert to Gibbs' notation and substitute p', p'', p''' for p_1, p_2, p_3.)

In this way the important conclusion emerges that only three fluid pressures are compatible with an assigned *homogeneous* state of strain of the solid in contact with the fluid, and if one of these pressures is established in the fluid, the solid, if equilibrium is to be preserved, can only be in contact with it at a pair of plane surfaces whose normals are opposite to one another in direction. Of course, this is a general statement; there are special cases where wider possibilities can exist. If, for instance, in the state of strain the three principal stresses are equal to one another, the "stress quadric" is a sphere; all sets of three axes are principal; there are no shearing stresses for any axes. (See case (3), Gibbs, I, bottom of page 195.) This is in fact the case of "hydrostatic stress" referred to frequently in these pages by Gibbs. In such a state the form of the solid does not matter. Immersed in a fluid throughout which there exists a constant pressure a solid will be in a homogeneous state of strain compatible with the condition of hydrostatic stress, that is, the condition in which there are no shears and the stress over any surface is normal to it and is of the pressure type. (The reader should not misconceive the phrase "*homogeneous* state of strain." This implies that a_{11}, a_{12}, ... a_{33} have values which are severally constant throughout the solid. But there is no implication, for instance, that $a_{11} = a_{22} = a_{33}$. It should be clearly recognized that this is not necessarily the case even for a state compatible with hydrostatic stress. It would be so, no doubt, if the solid were *isotropic* in nature; in that event all linear contractions or extensions would be equal and no shears would exist, but for crystalline solids the more general nature of the stress-strain relations would permit of wider conditions of strain, even if for any set of axes X_X, Y_Y, Z_Z were equal to one another, and the remaining stress-constituents zero.) If, however, one is to maintain the rectangular parallelopiped of solid material, imagined by Gibbs at this juncture, in equilibrium in a general homogeneous state of strain, one must arrange for different pressures on the different pairs of faces. So if the solid is in contact with a fluid of suitable pressure at one pair of opposite faces, it cannot be so at the other two pairs. It must be constrained by some other surface forces (pressural or tensional) on these faces to maintain the assigned state of strain. If these constraints are released and the fluid comes into contact with all six faces there will be an immediate change to another state of homogeneous strain compatible with the condition of hydrostatic stress. In such a change there will be a diminution of intrinsic energy of strain, since all release of constraints if followed by movement converts potential energy into kinetic energy of sensible masses, or heat. This justifies the brief statement of Gibbs on page 196 near the bottom: "This quantity is necessarily positive except, etc."

The remarks so far have been concerned with *mechanical* equilibrium. Equation [388], rewritten for the three possible pressures in [393], [394], [395] involves equilibrium as regards solution of the solid in the fluid, or crystallization on the solid from the fluid. This amplification of Gibbs' treatment of the mechanical relations will, it is hoped, render the task of mastering these pages easier for the reader; there appears to be nothing of special difficulty in the deductions on page 197 concerning the supersaturation of the fluid.

It should be carefully borne in mind that the argument has been confined to a *homogeneous* state of strain in the solid. Gibbs remarks on page 197 that "within certain limits the relations expressed by equations [393]–[395] must admit of realization." But even if it were hardly practicable to make the special arrangements conceived in these arguments, that does not invalidate the conclusions. We are all thoroughly familiar with "perfect engines," "perfectly smooth surfaces," "perfect gases" and other conceptual devices of the physicist and chemist which are the "stock in trade" of many mechanical and thermodynamical arguments. Of course in any practical case, if a solid of any form immersed in a fluid were subject to distorting surface forces the strain would be heterogeneous. Perhaps some readers, recalling equations (29) of this article or [377] of Gibbs, might wonder how a heterogeneous state of strain can exist without *body* forces; for in such a case the equations referred to would become

$$\frac{\partial X_X}{\partial x} + \frac{\partial X_Y}{\partial y} + \frac{\partial X_Z}{\partial z} = 0,$$

$$\frac{\partial Y_X}{\partial x} + \frac{\partial Y_Y}{\partial y} + \frac{\partial Y_Z}{\partial z} = 0,$$

$$\frac{\partial Z_X}{\partial x} + \frac{\partial Z_Y}{\partial y} + \frac{\partial Z_Z}{\partial z} = 0.$$

(We are neglecting gravity.) One might rashly conclude from these that $X_X, X_Y, \ldots X_Z$ must individually maintain constant values throughout the solid, and that the strains, therefore, being definite functions of these, would also be uniform in value throughout; but the conclusion is unwarranted, as the equations do not assert that each of the nine differential coefficients is zero. The torsion of a bar by gripping in the hands and twisting is an instance of heterogeneous strain under surface forces, which will be familar to all readers who have a special acquaintance with text-books of elasticity.

9. *Commentary on Pages 197–201. The Variations of the Temperature of Equilibrium with Respect to the Pressure and the Strains. The Variations of the Composition of the Fluid.* At the bottom of page 197, Gibbs begins an argument leading to equations [407] and [411]. Equation [407] is the analogue of the well-known equation, first discovered by James Thomson, giving the alteration in the melting point of a solid due to the increase of pressure on the surface. Perhaps if we put the analysis in a more general form than in the text it may assist the reader. We make no special arrangement about axes. The unit cube in the state of reference becomes in general, in the state of strain, an oblique parallelopiped whose volume has changed to $v_{V'}$, which as we have seen is equal to the determinant

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}.$$

A pair of opposite faces of the cube are in contact with the fluid in the state of reference and in the state of strain, so that one of the principal axes of stress is normal to this pair of faces of the oblique parallelopiped, the assigned homogeneous state of strain being maintained by suitable surface constraints on the remaining pairs of faces. Let there be an infinitesimal change *to a new condition of equilibrium*; this will involve changes of the strains to $a_{11} + da_{11}$, $a_{12} + da_{12}$, $\ldots$ $a_{33} + da_{33}$, of the fluid pressure to $p + dp$, of the temperature to $t + dt$, of the potential μ_1 to $\mu_1 + d\mu_1$, and of the energy and entropy of the solid to $\epsilon + d\epsilon$

and $\eta + d\eta$. There is no change in the mass of the solid, but its volume will change by an amount given by

$$dv_{V'} = A_{11}da_{11} + A_{12}da_{12} \ldots + A_{33}da_{33}.$$

This result depends on the fact that if the constituents of the determinant $|a|$, written above, are all altered by infinitesimal amounts, da_{11}, da_{12}, etc., then the infinitesimal change in the value of $|a|$ is equal to the expression on the right-hand side of the equation just written. Now by equation [355]

$$d\epsilon = td\eta + X_{X'}da_{11} + X_{Y'}da_{12} \ldots + Z_{Z'}da_{33}, \qquad [400a]$$

since for the postulated cube $\epsilon_{V'}$ and $\eta_{V'}$ are identical with ϵ and η. Also from [388]

$$d\epsilon = td\eta + \eta dt - pdv - vdp + md\mu_1, \qquad [401]$$

remembering that $v_{V'}$ is identical with v.

Equating [400a] and [401] we obtain

$$\left.\begin{aligned} \eta dt - vdp + md\mu_1 &= X_{X'}\,da_{11} + X_{Y'}\,da_{12} + \ldots \\ &\qquad + Z_{Z'}\,da_{33} + pdv \\ &= (X_{X'} + A_{11}\,p)\,da_{11} + (X_{Y'} + A_{12}\,p)\,da_{12} + \ldots \\ &\qquad + (Z_{Z'} + A_{33}\,p)\,da_{33}. \end{aligned}\right\}. \qquad [404a]$$

This is our form of equation [404]. If we then proceed to equation [405] which holds for a fluid identical in substance with the solid (so that we are dealing with fusion and solidification) we arrive at our form of [406], viz.,

$$\begin{aligned} (v_F - v)\,dp - (\eta_F - \eta)\,dt &= (X_{X'} + A_{11}\,p)\,da_{11} \\ + (X_{Y'} + A_{12}\,p)\,da_{12} \ldots &+ (Z_{Z'} + A_{33}\,p)\,da_{33}. \end{aligned} \qquad [406a]$$

In consequence we find that

$$\frac{\partial p}{\partial t} = \frac{Q}{t(v_F - v)}. \qquad [407]$$

Let us recall that p is the fluid pressure on a pair of opposite faces of the solid which is compatible with the given state of strain $a_{11}, a_{12}, \ldots a_{33}$. Thus p is a function of $a_{11}, a_{12}, \ldots a_{33}$ and the temperature; $\partial p/\partial t$ is therefore the rate of variation of this pressure with temperature *at constant strain,* i.e., with the solid constrained to keep its size and shape (in the state of strain) unchanged. This is the analogue of the usual equation for the variation of the melting point with pressure. The melting point is t at pressure p and strain $a_{11}, a_{12}, \ldots a_{33}$. At pressure $p + dp$ and the same strain $a_{11}, a_{12}, \ldots a_{33}$ the melting point is $t + dt$, the latent heat per unit volume is Q, and so $Q/t(v_F - v)$ is equal to the limit of dp/dt. It is necessary to realize the conditions under which Q is the latent heat of fusion. From [393] the energy of the solid with the proper pressure p' on a pair of faces is given by

$$\epsilon = t\eta - p'v + \mu_1'm.$$

That of the same mass of the fluid in equilibrium with the faces is given by

$$\epsilon_F = t\eta_F - p'v_F + \mu_1'm.$$

Hence

$$\epsilon_F - \epsilon = t(\eta_F - \eta) = Q.$$

As Gibbs points out, if we imagine the cube surrounded entirely by the fluid so that the conditions are those of the case usually considered, the quantities ϵ and η have different values from those considered above (see equations [396]), and Q is also different in value.

The more general case considered on page 200 when the fluid is not identical in substance with the solid can be followed up as is done by Gibbs, and we arrive at [411] in the form

$$\begin{aligned}&\left\{m\frac{\partial\mu_1\,(t,\,p,\,m_r)}{\partial p} - v\right\}dp\\ &+ m\left\{\frac{\partial\mu_1\,(t,\,p,\,m_r)}{\partial m_2}\,dm_2 + \frac{\partial\mu_1\,(t,\,p,\,m_r)}{\partial m_3}\,dm_3 + \text{etc.}\right\}\\ &= (X_{X'} + A_{11}\,p)\,da_{11} + (X_{Y'} + A_{12}\,p)\,da_{12}\ldots\\ &\qquad + (Z_{Z'} + A_{33}\,p)\,da_{33}.\end{aligned}$$

(In this $\mu_1(t, p, m_r)$ is a contraction for $\mu_1(t, p, m_1, m_2, m_3, \ldots)$ indicating the functional dependence of μ_1 on t, p, m_1, m_2, m_3, . . . ; m is of course the mass of the solid.) The treatment by Gibbs on pages 198–201 is based on certain geometrical postulates. In the state of reference he chooses lines parallel to the edges of his unit cube as axes of reference. In the state of strain he takes OZ to be perpendicular to the faces in contact with the fluid, i.e., to be one of the principal axes of stress. The other two axes OX, OY are of course in the plane containing the other two principal axes of stress, and one of them, OX, is chosen so as to be parallel to one of the edges of the oblique parallelopiped. Thus all points which have the same z'-coordinates in the state of reference have the same z-coordinates in the state of strain; in consequence z is a function of z' alone being independent of x' and y', and so a_{31} and a_{32} are zero. (See [398].) Moreover all points which have the same y' and z' coordinates in the state of reference, i.e., lie on a line parallel to OX', have the same y and z coordinates in the state of strain. Thus y is a function of y' and z' and is independent of x', and so a_{21} is also zero, (again see [398]). From this point on he pursues the analysis as above with the absence of certain terms which vanish on account of the conditions

$$a_{21} = a_{31} = a_{32} = 0.$$

Thus the determinant of the a_{rs} coefficients becomes

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & 0 & a_{33} \end{vmatrix}$$

which is just $a_{11}a_{22}a_{33}$ as in [402]. The reader will find no difficulty now in following the steps in the remaining three pages, having had these postulates explained and having followed the argument already in a more general manner.

Finally, before leaving this sub-section we shall refer to the remark at the top of page 199. The increase in the energy of the solid during the infinitesimal strain is as usual

$$X_{X'}da_{11} + X_{Y'}da_{12} \ldots + Z_{Z'}da_{33}.$$

This is of course equal to the work of all the surface forces during the variation of strain. These surface forces may be regarded as due to the pressure p on all the faces (a hydrostatic pressure) together with additional forces on four of the faces. The work of the hydrostatic pressure is $-pdv$ which is equal to

$$-p(A_{11}da_{11} + A_{12}da_{12} \ldots + A_{33}da_{33}).$$

Hence by subtracting this from the increase of energy of strain we obtain the work of the additional forces and this is seen to be equal to the right hand member of our [404a], and becomes the right hand side of [404] when Gibbs' special geometrical conditions are assumed.

10. Commentary on Pages 201-211. Expression of the Energy of a Solid in Terms of the Entropy and Six Strain-Coefficients. Isotropy. Having discussed the conditions of equilibrium Gibbs proceeds in the subsection on the *Fundamental Equations for Solids* to consider the problem of expressing the functional relationship between the energy per unit volume, the entropy per unit volume and the nine strain-coefficients. If $\epsilon_{V'}$ is expressed as a function of $\eta_{V'}, a_{11}, a_{12}, \ldots a_{33}$, or $\psi_{V'}$ is expressed as a function of $t, a_{11}, a_{12}, \ldots a_{33}$, we can by differentiation obtain, as we have already pointed out in this article, the stress-strain relations, which will be nine of the eleven independent relations referred to by Gibbs on page 203. He opens the subsection with some rather involved considerations on a special point, which we pass over for the moment, and then briefly touches on the fact that the energy or free energy functions must have a special form in the nine strain-coefficients, inasmuch as the strain of an element is capable of only six independent variations. This we have already explained in our discussion, where we chose the six quantities $f_1, f_2, \ldots f_6$ to represent the displacements arising from pure strain, as distinct from possible additional displacements involved in the nine coefficients $a_{11}, a_{12}, \ldots a_{33}$, which are the result of a pure rotation and produce no distortion of the material. The f_r quantities are themselves functions of the six quantities $e_1, e_2, \ldots e_6$ (or $a_1, a_2, \ldots a_6$) which are the same as A, B, C, a, b, c defined in [418], [419]. Thus the energy or free-energy functions must be functions of these six quantities, or in other words "the determination of the fundamental equation for a solid is thus reduced to the determination of the relation between $\epsilon_{V'}$, $\eta_{V'}$, A, B, C, a, b, c, etc." (page 205). Having pointed this out Gibbs at once proceeds to discuss a further limitation on the form of these functions if the solid is *isotropic,* and this involves him at once in an appeal to the existence of three principal axes of strain for any kind of material, a fact to which we have already referred in this article. Thereafter he deals with approximations to the form of these functions and concludes this subsection on that topic.

Let us proceed to the subject matter of pages 205–209 of the original which has been treated in our discussion in a somewhat different manner. The starting point of Gibbs' treatment is the equation [420] and this has already appeared implicitly in this article. For we know that if P' and Q' are the positions in the state of reference of two adjacent points, and P and Q are their positions in the state of strain, then

$$\overline{PQ}^2 = a_1\xi'^2 + a_2\eta'^2 + a_3\zeta'^2 + 2a_4\eta'\zeta' + 2a_5\zeta'\xi' + 2a_6\xi'\eta',$$

where x', y', z' and $x' + \xi'$, $y' + \eta'$, $z' + \zeta'$ are the coordinates of P' and Q' and a_1, a_2, a_3, a_4, a_5, a_6 are six functions of the strain coefficients defined in (23), or, as already stated, the same functions which Gibbs defines in [418] and [419] denoted by the symbols A, B, C, a, b, c, respectively. If α', β', γ' are the direction-cosines of $P'Q'$ with reference to the axes OX', OY', OZ' so that $\alpha' = \xi'/P'Q'$, etc., it follows that

$$a_1\alpha'^2 + a_2\beta'^2 + a_3\gamma'^2 + 2a_4\beta'\gamma' + 2a_5\gamma'\alpha' + 2a_6\alpha'\beta' = \frac{\overline{PQ}^2}{\overline{P'Q'}^2} = r^2$$

which is just Gibbs' equation [420].

The method pursued by Gibbs at this point to demonstrate the existence of the principal axes of strain employs the analytical processes associated with the discovery of maximum-minimum conditions of a function of several variables, and resembles that employed by him on pages 194, 195 when demonstrating the existence of the principal axes of stress. It will be followed easily by those versed in such analytical methods, but for other readers not so well acquainted with mathematical technique we can give a geometrical flavor to the argument which may prove helpful. We saw in the previous discussion that

$$a_1\xi'^2 + a_2\eta'^2 + a_3\zeta'^2 + 2a_4\eta'\zeta' + 2a_5\zeta'\xi' + 2a_6\xi'\eta' = k^2$$

is the equation of a locus drawn round the local origin P' which is strained into a sphere around the center P. This locus is an ellipsoid, and its actual form and the orientation of its principal axes in the body are of course dependent entirely on the magnitude and nature of the strain and not at all on the particular choice of the axes of reference, OX', OY', OZ'. We have already seen in this article that the principal axes of this "elongation ellipsoid" experience no shear and so are the principal axes of strain, and we can therefore proceed at once to the deduction of equations [430] and [431] on page 207. The method is well known to students of analytical geometry. Suppose that R' is a point in which one of the principal axes of this elongation ellipsoid through its center P' cuts the surface, and let its local coordinates be ξ_1', η_1', ζ_1'. We know that the direction cosines of the normal at P' are proportional to

$$a_1\xi_1' + a_6\eta_1' + a_5\zeta_1', \qquad a_6\xi_1' + a_2\eta_1' + a_4\zeta_1',$$
$$a_5\xi_1' + a_4\eta_1' + a_3\zeta_1'.$$

But since $P'R'$ is along a principal axis, the normal at R' coincides with $P'R'$ and so the direction cosines are also proportional to ξ_1', η_1', ζ_1'. Thus the three quantities

$$\frac{a_1\xi_1' + a_6\eta_1' + a_5\zeta_1'}{\xi_1'}, \qquad \frac{a_6\xi_1' + a_2\eta_1' + a_4\zeta_1'}{\eta_1'},$$
$$\frac{a_5\xi_1' + a_4\eta_1' + a_3\zeta_1'}{\zeta_1'},$$

have the same value. So it appears that if α', β', γ' are the direction cosines of any one of the three principal axes then

$$\begin{aligned} a_1\alpha' + a_6\beta' + a_5\gamma' &= \rho\alpha', \\ a_6\alpha' + a_2\beta' + a_4\gamma' &= \rho\beta', \\ a_5\alpha' + a_4\beta' + a_3\gamma' &= \rho\gamma', \end{aligned}$$

where ρ is a multiplier still undetermined, but the same in all three equations. These, combined with the equation $\alpha'^2 + \beta'^2 + \gamma'^2 = 1$, are sufficient to determine, first the value of ρ, and then the values of α', β', γ' in terms of the six strain-functions, a_1, a_2, ... a_6. The analysis is exactly similar to that which we employed earlier when explaining the conditions for the existence of a homogeneous strain in a solid in contact with a liquid. We write the preceding equations in the form

$$\left.\begin{aligned} (a_1 - \rho)\alpha' + a_6\beta' + a_5\gamma' &= 0, \\ a_6\alpha' + (a_2 - \rho)\beta' + a_4\gamma' &= 0, \\ a_5\alpha' + a_4\beta' + (a_3 - \rho)\gamma' &= 0. \end{aligned}\right\} \qquad [429a]$$

(The reader will easily satisfy himself that these are the equations [429] with ρ substituted for r^2.) Now, for reasons which we have already discussed in the place just referred to, these three equations are not consistent with one another unless the following determinantal equation is true:

$$\begin{vmatrix} a_1 - \rho & a_6 & a_5 \\ a_6 & a_2 - \rho & a_4 \\ a_5 & a_4 & a_3 - \rho \end{vmatrix} = 0,$$

and this is actually equation [430], with ρ substituted for r^2. It is of course a cubic equation in ρ and can be written, on expanding the determinant, as

$$\rho^3 - E\rho^2 + F\rho - G = 0,$$

where

$$E = a_1 + a_2 + a_3,$$

$$F = a_2a_3 + a_3a_1 + a_1a_2 - a_4{}^2 - a_5{}^2 - a_6{}^2,$$

$$G = \begin{vmatrix} a_1 & a_6 & a_5 \\ a_6 & a_2 & a_4 \\ a_5 & a_4 & a_3 \end{vmatrix}$$

$$= a_1a_2a_3 + 2a_4a_5a_6 - a_1a_4^2 - a_2a_5^2 - a_3a_6^2.$$

(See equations [431], [432] [433], [435].)

This equation in ρ has three roots ρ_1, ρ_2, ρ_3, functions of course of E, F and G; if one of these roots is substituted for ρ in any two of the equations [429a] above we can solve for the ratios α'/γ', β'/γ' and thus, using the condition $\alpha'^2 + \beta'^2 + \gamma'^2 = 1$, determine α', β', γ' for one of the axes; the remaining two values ρ_2, ρ_3 determine similarly the other two axes.

It remains to interpret the physical meanings of ρ_1, ρ_2, ρ_3, and that offers no difficulty. We saw above that if r is the ratio of elongation parallel to *any* direction α', β', γ' then

$$\begin{aligned} r^2 &= a_1\alpha'^2 + a_2\beta'^2 + a_3\gamma'^2 + 2a_4\beta'\gamma' + 2a_5\gamma'\alpha' + 2a_6\alpha'\beta' \\ &= (a_1\alpha' + a_6\beta' + a_5\gamma')\alpha' + (a_6\alpha' + a_2\beta' + a_4\gamma')\beta' \\ &\qquad + (a_5\alpha' + a_4\beta' + a_3\gamma')\gamma'. \end{aligned}$$

If now α', β', γ' is the direction of the first principal axis, then, since $a_1\alpha' + a_6\beta' + a_5\gamma' = \rho_1\alpha'$, etc., it follows that

$$\begin{aligned} r_1^2 &= \rho_1\alpha'^2 + \rho_1\beta'^2 + \rho_1\gamma'^2 \\ &= \rho_1. \end{aligned}$$

Similarly $\rho_2 = r_2^2$, $\rho_3 = r_3^2$. The remaining steps now follow easily. By the well-known relations between the roots and coefficients of an equation of integral order in one unknown we have

$$\begin{aligned} \rho_1 + \rho_2 + \rho_3 &= E, \\ \rho_2\rho_3 + \rho_3\rho_1 + \rho_1\rho_2 &= F, \\ \rho_1\rho_2\rho_3 &= G, \end{aligned}$$

and these are just equations [439], which we obtained in this article by another method. (As mentioned at that point a straightforward, if tedious, piece of algebra will show that

$$a_2a_3 + a_3a_1 + a_1a_2 - a_4^2 - a_5^2 - a_6^2$$
$$= A_{11}^2 + A_{12}^2 \dots + A_{33}^2,$$

where A_{pq} is the first minor of a_{pq} in the determinant of the coefficients, viz. H. This gives the alternative expression for F in [434]. Also, we have already seen that the rule for multiplying determinants will verify that $H^2 = G$.) A rather special point is raised and disposed of on pages 210, 211. It concerns the sign of the determinant H. It is clear from [439] that G is a positive quantity, but H may, of course, have a negative value instead of a positive one from a *purely mathematical* standpoint; but from a physical standpoint negative values of H are ruled out, provided we agree that the axes OX', OY', OZ' and OX, OY, OZ *are capable of superposition,* meaning that if the latter are turned so that OX points along OX', and OY along OY', then OZ will point along OZ' (not along $Z'O$). In short, if one set of axes is "right-handed" the other must be likewise, if one is "left-handed," so also is the other. (A right-handed set of axes is one so oriented that to an observer looking in the direction OZ', a right-handed twist would turn OX' to OY', etc.) Gibbs illustrates this by considering a displacement of the particles which is represented by

$$x = x', \qquad y = y', \qquad z = -z',$$

the two sets of axes being regarded as identical. (If they were not they could easily be made so by a rotation.) Now the H determinant of this is

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix},$$

whose value is -1. But such a displacement is one which moves every particle to the position of its "mirror image" with respect to a mirror imagined as located in the plane $z' = 0$, i.e,

$OX'Y'$. This displacement cannot be effected by any simple rotation. (A rotation of the body for example round the axis of OX' through two right angles would be represented by the equations

$$x = x', \qquad y = -y', \qquad z = -z'$$

whose H determinant has the value $+1$.) Indeed, to produce the displacement indicated we would have to conceive a continuous distortion of the body in which all the particles of the body would have to be gradually "squeezed" towards the plane $OX'Y'$, the body growing flatter and more "disc-like" until it is squeezed to a limiting volume zero; thereupon it would begin to swell again to the same size as before, but with all the particles previously on the positive side of the plane $OX'Y'$ now on the negative, and *vice-versa*. Such a process while conceivable is hardly possible physically. It should be noted that in the course of such a conceptual *continuous* process the volume would pass through the value zero; also the determinant H, which is the ratio of volume dilatation, would pass through decreasing small values from unity to zero, then change to negative values and grow *numerically* (decreasing algebraically) to the limiting value -1, as we indicated above. This short discussion will perhaps help the reader while perusing pages 210, 211.

We now revert to the short paragraph beginning near the top of page 205 with the words "In the case of isotropic bodies." Unless the reader is on his guard the position of this paragraph in the general argument might unconsciously incline his mind to the view that the subsequent discussion concerning principal axes of strain is only valid for isotropic solids, and this would be unfortunate. Nothing in Gibbs' own argument nor in that given earlier in this article warrants such a restriction. No matter what the nature of the solid, any group of external forces will produce a distortion and a system of stresses such that there are in any element three principal axes of strain for which the shearing strain-coefficients e_4, e_5, e_6 vanish, and three principal axes of stress for which the stress-constituents Y_Z (or Z_Y), Z_X (or X_Z), X_Y (or Y_X) vanish. If the strain is homogeneous the principal axes of strain are oriented alike in all elements; that will also be true of the principal axes of stress *if in addition the body is homogeneous in nature.* But it will naturally occur to the reader to inquire whether the principal axes of strain are coincident with those of stress, and indeed this query and its answer is just the matter at issue at this point in Gibbs' text. A few lines before, Gibbs refers to the now familiar fact that the state of strain (as distinct from rotation) is given by *six* functions of the strain-coefficients a_{11}, a_{12}, . . . a_{33}, choosing, for reasons now fully discussed, a_1, . . . a_6 as these functions (or A, B, C, a, b, c, as he styles them) and points out that for any material, homogeneous in nature or not, isotropic or not, the energy per unit volume will be a function of the entropy per unit volume and the six strain-functions. This we have already discussed in the present article. For *isotropic* materials, however, there is a certain simplification, *three* functions of the strain-coefficients being sufficient for this purpose. Gibbs derives this result from the sentence at the end of the short paragraph referred to above, namely the sentence: "*If the unstrained element is isotropic*" (the italics are the writer's) "the ratios of elongation for these three lines must with $\eta_{V'}$ determine the value of $\epsilon_{V'}$." Now this is hardly obvious without some further consideration of the meaning of isotropy in this connection. Space does not permit us to discuss the matter fully, but the central idea can be indicated. The essential character of an elastically isotropic solid is embodied in two facts.

1. For any system of external forces the principal directions of stress in any element are identical with the principal directions of strain.

2. The number of elastic constants required to express the relations between stress and strain *for small strains* is two.

Thus if we take the axes of reference to be parallel to these principal directions, we have the extremely simple stress-strain relations (in the conventional text-book form)

$$\begin{aligned} X_X &= \lambda\delta + 2\mu e_{11}, \\ Y_Y &= \lambda\delta + 2\mu e_{22}, \\ Z_Z &= \lambda\delta + 2\mu e_{33}. \end{aligned}$$

In these equations λ and μ represent the two elastic constants, δ is the sum of e_{11}, e_{22}, e_{33} being known as the "dilatation." (e_{23}, e_{32}, e_{31}, e_{13}, e_{12}, e_{21} as well as Y_Z, Z_X, X_Y are zero.) The various moduli can be expressed in terms of λ and μ. (In fact μ happens to be the modulus of rigidity itself.)

Indeed the idea of isotropy may be broadly indicated by reverting to an illustration which we gave in a rather vague form at the outset of our exposition. Imagine a system of forces to be exerted on a body, *spherical in shape*, at definite points of the body. These will produce a system of strains and stresses. In a given element there will be a common triad of principal directions. Now conceive the body to be rotated round its center to another orientation, but conceive also that the same forces as before are acting, not at the same points *in the body*, but at the same points *in the frame of reference*, i.e., points with the same coordinates with respect to the axes of reference, which we regard as fixed. Exactly the same system of stresses and strains will be produced as before. This does not mean that the element referred to above (i.e., the element occupying the same situation *in the body*) will be strained just as before; but the element of the body occupying the same situation *in the frame of reference* will experience the same strains and stresses as were experienced previously by the element originally in that situation, with the same orientation for the principal axes. (It must be carefully borne in mind that this is true for *isotropic* bodies only; in fact it constitutes a definition of isotropy in elastic properties.) The energy of the spherical body after the rotation is the same as before. This gives us the key to the situation. Such a rotation would be equivalent *mathematically* to referring a strained body first to any axes of reference (not necessarily principal axes of stress or strain) and then referring to another set; equivalent in fact to what the mathematician calls a "transformation of axes." The values of the strain-coefficients and strain-functions will change. In the first set of axes OX', OY', OZ', a_1, a_2, a_3, a_4, a_5, a_6 are the strain-functions and ξ', η', ζ' the local coordinates. The elongation-ellipsoid is

$$a_1\xi'^2 + a_2\eta'^2 + a_3\zeta'^2 + 2a_4\eta'\zeta' + 2a_5\zeta'\xi' + 2a_6\xi'\eta' = k^2.$$

Now we rotate the axes of reference to OL', OM', ON'. Let the strain-functions for these axes now be α_1, α_2, α_3, α_4, α_5, α_6 and the local coordinates λ', μ', ν'. Of course α_1 is not in general equal to a_1, nor α_2 to a_2, etc.; for $\alpha_1^{\frac{1}{2}}$ is the ratio of elongation parallel to OL', while $a_1^{\frac{1}{2}}$ is that parallel to OX', etc.; and $\alpha_6/(\alpha_1\alpha_2)^{\frac{1}{2}}$ is the shear of OL' and OM' while $a_6/(a_1a_2)^{\frac{1}{2}}$ is the shear of OX' and OY', etc. But the equation

$$\alpha_1\lambda'^2 + \alpha_2\mu'^2 + \alpha_3\nu'^2 + 2\alpha_4\mu'\nu' + 2\alpha_5\nu'\lambda' + 2\alpha_6\lambda'\mu' = k^2$$

represents just the same elongation-ellipsoid as before, situated in the same *way* in the body. Let the function which expresses the strain energy in terms of $a_1, a_2, \ldots a_6$ be $\phi(a_1, a_2, \ldots a_6)$. Exactly the same function of $\alpha_1, \alpha_2, \ldots \alpha_6$ must also be equal to the strain energy. This must be so *on account of the isotropy.* In the illustration above, assume the sphere to be strained homogeneously for simplicity, and refer to any axes of reference. Keeping the forces as it were "in situ," we rotate the sphere *and axes.* The energy is unchanged. But the mathematical considerations leading us to a certain function of $a_1, a_2, \ldots a_6$ which is equal in value to the energy will lead us in the second case to just the same function of $\alpha_1, \alpha_2, \ldots \alpha_6$; for the general operations are unchanged by a change of axes and just the same relations exist between the stress-constituents and the strain-coefficients for any one set of axes as for another. Once more that is the essence of isotropy.

We are thus naturally led at once to the purely mathematical question of trying to solve the following problem:

"An ellipsoid referred to OX', OY', OZ' has the equation

$$a_1\xi'^2 + a_2\eta'^2 + a_3\zeta'^2 + 2a_4\eta'\zeta' + 2a_5\zeta'\xi' + 2a_6\xi'\eta' = k^2.$$

When referred to another set of axes OL', OM', ON' its equation is

$$\alpha_1\lambda'^2 + \alpha_2\mu'^2 + \alpha_3\nu'^2 + 2\alpha_4\mu'\nu' + 2\alpha_5\nu'\lambda' + 2\alpha_6\lambda'\mu' = k^2.$$

What function of a_1, a_2, a_3, a_4, a_5, a_6 is equal in value to the same function of α_1, α_2, α_3, α_4, α_5, α_6?"

That problem we have implicitly solved in the note on quadric surfaces (see Article B of this volume). For there we have mentioned, with references to sources, the fact that it can be proved that

$$a_1 + a_2 + a_3 = \alpha_1 + \alpha_2 + \alpha_3,$$

$$a_2a_3 + a_3a_1 + a_1a_2 - a_4^2 - a_5^2 - a_6^2$$
$$= \alpha_2\alpha_3 + \alpha_3\alpha_1 + \alpha_1\alpha_2 - \alpha_4^2 - \alpha_5^2 - \alpha_6^2,$$

$$\begin{vmatrix} a_1 & a_6 & a_5 \\ a_6 & a_2 & a_4 \\ a_5 & a_4 & a_3 \end{vmatrix} = \begin{vmatrix} \alpha_1 & \alpha_6 & \alpha_5 \\ \alpha_6 & \alpha_2 & \alpha_4 \\ \alpha_5 & \alpha_4 & \alpha_3 \end{vmatrix}.$$

Thus we see that there are three fairly simple functions which enjoy the property referred to in the enunciation; and of course any given function of these three functions will also have the property. Thus the strain energy of an isotropic body per unit volume must be expressible in terms of the three functions written above on either side of the equality sign. These functions are in fact E, F, G of the text. The upshot of the argument is that, while for any material the strain-energy per unit volume is a function of the strain-functions a_1, a_2, a_3, a_4, a_5, a_6, it can be shown that for isotropic material the function has a special form, being a function of three special functions of the strain-functions. Gibbs' own argument, based, as we stated, on the sentence from page 205 quoted above, assumes that the strain-energy is solely dependent on r_1, r_2, r_3 (and temperature), and of course by reason of [439] these are functions of E, F, G. As he himself remarks on page 209, although we could regard the strain-energy per unit volume as a function of r_1, r_2, r_3 "it will be more simple to regard $\epsilon_{V'}$ as a function of $\eta_{V'}$ and the quantities E, F, G." It seems therefore to the writer not out of place to have put the argument on grounds which do not directly involve the principal elongations and which appeal to general ideas of isotropy. The argument outlined above does not apply to an aeolotropic (anisotropic) body. We cannot afford space to go into this further but must refer the reader to standard texts on elasticity or to Goranson's book* on this matter. For one thing, in an aeolotropic body the principal direction of stress and those of strain do not in general coincide, and if we carried out the conceptual experiment suggested above of rotating a spherical body keeping the forces and their points of application "in situ" in the frame of reference, the strains and stresses would not in general be same in an element as they were previously in the element which originally was situated in the same place in the frame of reference; for the *orientation* of the two elements would be different although their relation to the external forces would be the same, and that would be a significant change for an aeolotropic element, even although the two elements were homogeneous in nature. Hence the rotation would in general involve an entire alteration in the general state of stress and strain and a change of strain-energy. Thus one of the premises of the argument would collapse.

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* See p. 433 of this article.

We have already referred to the arguments by which Gibbs justifies the use of the determinant H (with a positive value) instead of G for expressing the energy of an isotropic material.

11. Commentary on Pages 211–214. Approximative Formulae for the Energy and Free Energy in the Case of an Isotropic Solid. The approximative formulae given by Gibbs in [443] and [444] are just examples of the expansion of a function in series by the use of Taylor's theorem, neglecting powers higher than the first. For small strains r_1, r_2, r_3 differ little from unity. By [439] E differs little from 3, F from 3, and G or H from unity. Writing E' for $E - 3$, F' for $F - 3$, and H' for $H - 1$, we can express any function of E, F, H as a function of E', F', H'. We can expand this function as a series by Taylor's theorem, say

$$k + aE' + bF' + cH' + \text{higher powers and products of } E', F', H'.$$

For small strains the higher powers and products are negligible compared to the terms involving the first power. So to the first approximation the function will be

$$l + aE + bF + cH$$

(where $l = k - 3a - 3b - c$), which has the form of [443] or [444].

The justification of [445] can be easily given as follows. Remembering that $\psi_{V'}$ is a function of E, F, H, say $\phi(E, F, H)$, it follows that

$$\frac{\partial \psi_{V'}}{\partial r_1} = \frac{\partial \phi}{\partial E}\cdot\frac{\partial E}{\partial r_1} + \frac{\partial \phi}{\partial F}\cdot\frac{\partial F}{\partial r_1} + \frac{\partial \phi}{\partial H}\cdot\frac{\partial H}{\partial r_1}$$

$$= 2r_1\frac{\partial \phi}{\partial E} + 2r_1\,(r_2^2 + r_3^2)\,\frac{\partial \phi}{\partial F} + r_2 r_3\frac{\partial \phi}{\partial H}.$$

Similarly

$$\frac{\partial \psi_{V'}}{\partial r_2} = 2r_2\frac{\partial \phi}{\partial E} + 2r_2\,(r_3^2 + r_1^2)\,\frac{\partial \phi}{\partial F} + r_3 r_1\frac{\partial \phi}{\partial H}.$$

Obviously

$$\frac{\partial \psi_{V'}}{\partial r_1} = \frac{\partial \psi_{V'}}{\partial r_2}$$

if $r_1 = r_2 = r_3$, and exactly similar arguments cover the other equations. The wording of the argument at this point on page 212 is a little confusing; for, as the text itself points out, this theorem is true "if $\psi_{V'}$ is any function of t, E, F, H," not merely the approximative linear function of [444]; then just lower down we have references to "proper" and "true" values of $\psi_{V'}$. It might be better therefore to introduce two functional symbols one $\phi(t, E, F, H)$ to refer to the "true" value of $\psi_{V'}$ and one $\chi(t, E, F, H)$ to refer to the linear function of E, F, H in [444] which is approximately equal to $\psi_{V'}$. These can both be expanded as series in terms of r_1, r_2, r_3, or rather of $r_1 - r_0$, $r_2 - r_0$, $r_3 - r_0$; the discussion centers round the problem of determining at what power of $r_1 - r_0$, etc., the two series begin to show a difference. A little thought will show that the series for χ will terminate at fourth order terms. In fact writing for the moment x for $r_1 - r_0$, y for $r_2 - r_0$, z for $r_3 - r_0$, we see that

$$\begin{aligned}\chi = i &+ e\{(x + r_0)^2 + (y + r_0)^2 + (z + r_0)^2\}\\ &+ f\{(y + r_0)^2(z + r_0)^2 + (z + r_0)^2(x + r_0)^2 +\\ &\qquad (x + r_0)^2(y + r_0)^2\}\\ &+ h(x + r_0)\,(y + r_0)\,(z + r_0).\end{aligned}$$

The series therefore involves first powers and squares of x, y, z and product terms such as xy, xyz, x^2y, x^2y^2. Of course the series for ϕ will in general extend beyond such terms and may indeed be a convergent infinite series. Before proceeding further, it might be well to point out that r_0 is just an ordinary factor of temperature expansion (linear), resembling in fact the familiar $1 + at$ of the text-book of heat. It is necessary to bear in mind that the state of reference is a state at a given original temperature. If the solid is warmed (or cooled) to another temperature *without any application of external forces and creation of stress,* straining takes place; for an isotropic material it is a uniform expansion. This is an excellent illustration of the necessity of keeping the notions of strain and of stress clearly separated in the mind. Our instinctive notions of pulling, pushing, twisting, bending bodies into different shapes and sizes gives us an unconscious bias towards the idea that stress must invariably accompany strain and vice-versa, whereas change of temperature produces strain (change of size at all events, if not a change of shape which generally accompanies heating of crystalline material) without stresses being created, and if we prevent the strain occurring we have to exert external force on the body with the creation of internal stress, sometimes of relatively enormous value. (We can all recall the experiment in our lecture course in elementary physics when the demonstrator fractured the red-hot bar, or the clamps which held it tightly at its ends, by pouring cold water over it.) If therefore we alter the temperature of the (isotropic) body and subject it to external force, the principal elongations with reference to the *unstressed* state of reference *at this temperature* will be r_1/r_0, r_2/r_0, r_3/r_0; and $\psi_{V'}$, regarded as a function of the temperature and the elongations, can be considered as expanded by Taylor's theorem in the form of a series in the relatively small variables $(r_1/r_0) - 1$, $(r_2/r_0) - 1$, $(r_3/r_0) - 1$. This comes to the same thing as regarding $\psi_{V'}$ (either its "true" value $\phi(t, E, F, H)$ or its approximative value $\chi(t, E, F, H)$) expanded as a series in $r_1 - r_0$, $r_2 - r_0$, $r_3 - r_0$.

Let ϕ_0, χ_0 be the values of ϕ and χ when r_0 is substituted for each of the quantities r_1, r_2, r_3 in E, F, H. Let $(\partial\phi/\partial r)_0$,

$(\partial^2\phi/\partial r^2)_0$, $(\partial^2\phi/\partial r\partial r')_0$ be the common values, assumed according to [445] by the various first and second differential coefficients of ϕ with respect to the variables r_1, r_2, r_3. Use a similar notation for χ. Then if we write down

$$\chi_0 = \phi_0,$$

$$\left(\frac{\partial\chi}{\partial r}\right)_0 = \left(\frac{\partial\phi}{\partial r}\right)_0,$$

$$\left(\frac{\partial^2\chi}{\partial r^2}\right)_0 = \left(\frac{\partial^2\phi}{\partial r^2}\right)_0,$$

$$\left(\frac{\partial^2\chi}{\partial r\partial r'}\right)_0 = \left(\frac{\partial^2\phi}{\partial r\partial r'}\right)_0,$$

we have four simultaneous equations to determine the *four* quantities i, e, f, h; these, as the text says, will give to the approximations χ, $\partial\chi/\partial r_1$, $\partial\chi/\partial r_2$, $\partial\chi/\partial r_3$, ... $\partial^2\chi/\partial r_1\partial r_2$ their "proper," i.e., correct, values ϕ, $\partial\phi/\partial r_1$, $\partial\phi/\partial r_2$, $\partial\phi/\partial r_3$, ... $\partial^2\phi/\partial r_1\partial r_2$ when $r_1 = r_2 = r_3 = r_0$, i.e., when the solid is in its unstressed state not at the original temperature of the state of reference but at the temperature for which it has expanded (or contracted) from that state in the ratio r_0. But by Taylor's theorem, if we expand ϕ in terms of $r_1 - r_0$, $r_2 - r_0$, $r_3 - r_0$, we have

$$\begin{aligned}\phi = \phi_0 &+ \left(\frac{\partial\phi}{\partial r_1}\right)_0 (r_1 - r_0) + \left(\frac{\partial\phi}{\partial r_2}\right)_0 (r_2 - r_0) + \left(\frac{\partial\phi}{\partial r_3}\right)_0 (r_3 - r_0)\\ &+ \frac{1}{2!}\left\{\left(\frac{\partial^2\phi}{\partial r_1^2}\right)_0 (r_1 - r_0)^2 + \left(\frac{\partial^2\phi}{\partial r_2^2}\right)_0 (r_2 - r_0)^2 + \left(\frac{\partial^2\phi}{\partial r_3^2}\right)_0 (r_3 - r_0)^2\right.\\ &+ 2\left(\frac{\partial^2\phi}{\partial r_2\partial r_3}\right)_0 (r_2 - r_0)(r_3 - r_0) + 2\left(\frac{\partial^2\phi}{\partial r_3\partial r_1}\right)_0 (r_3 - r_0)(r_1 - r_0)\\ &\left.+ 2\left(\frac{\partial^2\phi}{\partial r_1\partial r_2}\right)_0 (r_1 - r_0)(r_2 - r_0)\right\} + \text{higher powers}\\ = \phi_0 &+ \left(\frac{\partial\phi}{\partial r}\right)_0 (r_1 + r_2 + r_3 - 3r_0)\end{aligned}$$

$$+\frac{1}{2!}\left\{\left(\frac{\partial^2\phi}{\partial r^2}\right)_0[(r_1-r_0)^2+(r_2-r_0)^2+(r_3-r_0)^2]\right.$$

$$+2\left(\frac{\partial^2\phi}{\partial r\partial r'}\right)_0[(r_2-r_0)(r_3-r_0)+(r_3-r_0)(r_1-r_0)$$

$$\left.+(r_1-r_0)(r_2-r_0)]\right\}+\text{higher powers},$$

and similarly

$$\chi=\chi_0+\left(\frac{\partial\chi}{\partial r}\right)_0(r_1+r_2+r_3-3r_0)$$

$$+\frac{1}{2!}\left\{\left(\frac{\partial^2\chi}{\partial r^2}\right)_0[(r_1-r_0)^2+(r_2-r_0)^2+(r_3-r_0)^2]\right.$$

$$+2\left(\frac{\partial^2\chi}{\partial r\partial r'}\right)_0[(r_2-r_0)(r_3-r_0)+(r_3-r_0)(r_1-r_0)$$

$$\left.+(r_1-r_0)(r_2-r_0)]\right\}+\text{higher powers}.$$

Hence $\phi(t, E, F, H)$ and $\chi(t, E, F, H)$, the true and the approximative expansions of $\psi_{V'}$ agree to the terms of the second degree *inclusive.* The remaining statements on page 212 can be deduced similarly.

The equations

$$r_1^2+r_2^2+r_3^2=a_{11}^2+a_{12}^2+a_{13}^2+a_{21}^2+a_{22}^2+a_{23}^2$$
$$+a_{31}^2+a_{32}^2+a_{33}^2,$$

$$r_2^2r_3^2+r_3^2r_1^2+r_1^2r_2^2=A_{11}^2+A_{12}^2+A_{13}^2+A_{21}^2+A_{22}^2$$
$$+A_{23}^2+A_{31}^2+A_{32}^2+A_{33}^2,$$

$$r_1r_2r_3=\begin{vmatrix}a_{11}&a_{12}&a_{13}\\a_{21}&a_{22}&a_{23}\\a_{31}&a_{32}&a_{33}\end{vmatrix},$$

are equations [432], [434], [437] of the text. By partial differentiation with respect to a_{11}, we can, as Gibbs points out, regard the three quantities $\partial r_1/\partial a_{11}$, $\partial r_2/\partial a_{11}$, $\partial r_3/\partial a_{11}$ as determined by the resulting three simultaneous equations in these quantities (determined, i.e., in terms of the a_{pq} coefficients). Similar statements are true for any of the partial differential coefficients $\partial r_1/\partial a_{pq}$, $\partial r_2/\partial a_{pq}$, $\partial r_3/\partial a_{pq}$. These are of course correct values and have nothing to do with the approximation to $\psi_{V'}$ made in [444]. Now $X_{X'}$ is determined as we know by the equation

$$X_{X'} = \frac{\partial \psi_{V'}}{\partial a_{11}}.$$

(See equation, $\delta\psi_{V'} = \sum_p \sum_q (X_{X'} \delta a_{pq})$, near the top of page 204.) Since $\partial(r_1 - r_0)^n/\partial a_{11} = n(r_1 - r_0)^{n-1}\partial r_1/\partial a_{11}$, etc., we can express $X_{X'}$ as an ascending series in the quantities $r_1 - r_0$, $r_2 - r_0$, $r_3 - r_0$, and since the true and the approximative series for $\psi_{V'}$ agree to the second degree, the true and approximative series for $X_{X'}$ will agree to the first degree, and the error in $X_{X'}$ involved in using the approximative series will be of the order of magnitude of the squares of $r_1 - r_0$, $r_2 - r_0$, $r_3 - r_0$.

On pages 213, 214, e, f, h are determined in terms of the bulk-modulus and the modulus of rigidity. These two moduli, as we have mentioned earlier, possess physical significance only in so far as Hooke's law is obeyed; and this, as experiment demonstrates, restricts the range of stress allowable from the unstressed state at a given temperature. Gibbs' calculations on page 213 are limited by this consideration, as he himself expressly admits; for he indicates that his moduli are determined for "states of vanishing stress," and in the final results he goes to the limit at which $r_1 = r_2 = r_3 = r_0$; r_0 as before being the uniform ratio of elongation due to the change from the temperature for the state of reference (regarded as unstressed) to the temperature indicated by t. The formula for the bulk-modulus in [448] we have discussed earlier. To use it we must express p as a function of v and t. Consider a mass of the solid which has unit volume in the state of reference. It is subjected to the change of temperature which gives it the volume r_0^3. It is now subject to uniform pressure p which gives it a uniform elongation with the ratio r_1 in all directions *as compared with the state of reference at the original temperature,* so that its volume is now r_1^3 ($r_1 = r_2 = r_3$). Thus $E = 3r_1^2 = 3v^{\frac{2}{3}}$; $F = 3r_1^4 = 3v^{\frac{4}{3}}$; $H = r_1^3 = v$, and so we arrive at [451]. By equation [88] from the earlier part of Gibbs' discussion we obtain the general expression for p in [452] in any state of uniform stress small enough to be consistent with Hooke's law. Differentiation gives us [453], and an approach to the limit at which $v = r_0^3$ gives us the result [454].

The writer is unable to justify the equation [449] as it stands; as far as he can judge it ought to read

$$R = r_0 \frac{\partial X_{Y'}}{\partial a_{12}}.$$

To see this, let us consider the matter from the point of view of the ordinary treatment of isotropic solids in the text-books of elasticity. Limiting ourselves to strains so small that Hooke's law applies, the modulus of rigidity is defined as the common value of the quotients

$$\frac{Y_Z}{f_4},\ \frac{Z_X}{f_5},\ \frac{X_Y}{f_6}.$$

The quantities f_4, f_5, f_6 are the shears of the lines parallel to axes of reference (the same axes for the state of strain as for the state of reference). As we saw in our discussion the value of f_6, for example, is $e_6/(e_1e_2)^{\frac{1}{2}}$, although it can be replaced by an approximation $e_{12} + e_{21}$ for very small strains. This, of course, implies that changes of temperature are not involved. Let us, however, consider the situation which arises when the state of strain is at a temperature t, different from the temperature of the state of reference. The definition of the modulus of rigidity at temperature t must of course involve the shears of the axes from an unstressed state also at that temperature, that is, a state in which all lengths are elongated in the ratio r_0 as compared with the state of reference. The definition of R is still X_Y/f_6 (say), and f_6 is still $e_6/(e_1e_2)^{\frac{1}{2}}$. But we have to be careful about the approximation. Let us recall the definitions of

$e_1, e_2, \ldots e_6$ from this article or from [418], [419] of Gibbs:

$$e_6 = e_{11}e_{12} + e_{21}e_{22} + e_{31}e_{32},$$

$$e_1 = e_{11}^2 + e_{21}^2 + e_{31}^2,$$

$$e_2 = e_{12}^2 + e_{22}^2 + e_{32}^2.$$

In making the approximations we take as usual $e_{23}, e_{32}, e_{31}, e_{13}, e_{12}, e_{21}$ to be very small compared to e_{11}, e_{22}, e_{33}; but the three latter quantities do not now approximate to unity, as formerly, but to r_0, since in the unstressed state at temperature t, there exist elongations of amount r_0 as compared with the state of reference. Hence the approximations now must involve replacing e_6 by $r_0(e_{12} + e_{21})$, e_1 by r_0^2, e_2 by r_0^2.
Hence

$$f_6 \doteqdot \frac{e_{12} + e_{21}}{r_0}.$$

Thus

$$R = \frac{X_Y}{f_6} \doteqdot r_0 \frac{X_Y}{e_{12} + e_{21}}.$$

As we are assuming that the range of stress and strain is covered by Hooke's law it is also true that

$$R = r_0 \frac{X_Y + \delta X_Y}{e_{12} + \delta e_{12} + e_{21}},$$

where δX_Y is a small change of shearing stress produced by a small change δe_{12} in the coefficient e_{12}, and thus

$$R = r_0 \frac{\delta X_Y}{\delta e_{12}}.$$

This corresponds to Gibbs' equation [449] but with the r_0 on the right hand side of the equation, not on the left. The symbol r_0 can be obtained on the left if e_6 is taken as the approximation to f_6 (which is the case when change of temperature is not involved since e_{11} and e_{22} are then approximately unity); for if this is done and we write $r_0(e_{12} + e_{21})$ for f_6 we obtain Gibbs' result. But this amounts to putting e_{11} or e_{22} equal to unity in one part of the complete formula for f_6 and equal to r_0 in another. We should obviously approximate from $e_6/(e_1 e_2)^{\frac{1}{2}}$ and not from e_6.

If the writer is correct, then we should write equation [449] as

$$R = r_0 \frac{\partial X_{Y'}}{\partial a_{12}} \qquad [449a]$$

with of course $a_{11} = a_{22} = a_{33} = r_0$ and the remaining a_{pq} coefficients put equal to zero; for we are considering the value of R for the state of vanishing stress. This will change equations [455] and [457]. Thus

$$\psi_{V'} = i + e\Sigma\Sigma a_{pq}{}^2 + f\Sigma\Sigma A_{pq}{}^2 + hH,$$

and we have to differentiate this partially twice with respect to a_{12}. The term multiplied by e will yield $2e$. In the term which is multiplied by f, four of the A_{pq} minors involve a_{12}, viz., $A_{33}{}^2$, $A_{31}{}^2$, $A_{23}{}^2$, $A_{21}{}^2$, so that this term yields

$$2f\left\{A_{33}\frac{\partial A_{33}}{\partial a_{12}} + A_{31}\frac{\partial A_{31}}{\partial a_{12}} + A_{23}\frac{\partial A_{23}}{\partial a_{12}} + A_{21}\frac{\partial A_{21}}{\partial a_{12}}\right\}.$$

On passing to the limit when a_{23}, a_{32}, a_{31}, a_{13}, a_{12}, a_{21} are zero and $a_{11} = a_{22} = a_{33} = r_0$ it will be easily seen that the only surviving part of the derivations from this term is $2fA_{21}\,(\partial A_{21}/\partial a_{12})$ which becomes $2fa_{33}{}^2$ or $2fr_0{}^2$. Hence [449a] becomes

$$R = 2er_0 + 2fr_0{}^3, \qquad [455a]$$

which replaces [455]. It will then appear that in place of [457] we shall find

$$\left.\begin{aligned} e &= \tfrac{1}{3}\frac{R}{r_0} - \tfrac{1}{2}Vr_0, \\ f &= \tfrac{1}{6}\frac{R}{r_0{}^3} + \tfrac{1}{2}\frac{V}{r_0}, \\ h &= -\tfrac{4}{3}\frac{R}{r_0{}^2} - V. \end{aligned}\right\} \qquad [457a]$$

Similar changes will have to be made in [459] and [461], if the writer's emendation of [449] is correct.

Before leaving this subsection we shall revert for a moment to the special point passed over at the beginning of the commentary on this part. Pages 201 and 202 are rather involved but the point appears to be as follows. It has been implied hitherto that no particular physical properties are imposed on the state of reference. In ordinary elementary discussions in the text-books it is taken as unstressed, i.e., without any strain energy. Thus if a relation is given between $\epsilon_{V'}$ and $\eta_{V'}$, a_{11}, a_{12}, ... a_{33}, then $\epsilon_{V'}$ is the intrinsic energy of the state of strain; but if no such restriction is imposed on the state of reference then, since the coefficients a_{11}, a_{12}, ... a_{33} express a relation between the state of strain and the state of reference, the function $\epsilon_{V'}$ will give the excess of energy in the former state over the latter for the material occupying unit volume in the latter. Provided the state of reference is at all events one of homogeneous strain, this introduces no difficulties since the energy in any element of the solid in the state of reference is the same as that in any other, and therefore $\epsilon_{V'}$ differs from the intrinsic energy in the state of strain (per unit volume of the state of reference) by a constant amount, (i.e., the same for all elements of volume). But if, as Gibbs suggests, it happens that in some cases it is impossible to bring all elements in the state of reference simultaneously into the same state of strain, this means that in the state of reference the energy in an element depends on its position in the state of reference, i.e., on the coordinates of the point which it surrounds. We can, however, take some particular element in the state of reference as being in what we may call a "standard state." The condition in any other element in the state of reference can be stated in terms of the strain-coefficients which give the relation between the state of this latter element and the standard state, and the energy in this element in the state of reference will, apart from a constant, be a function of these latter strain-coefficients. Thus $\epsilon_{V'}$ will now be a function not only of the strain-coefficients a_{11}, a_{12}, ... a_{33} (connecting the state of strain with the state of reference) but also of other strain-coefficients connecting the state of reference with the standard state (which will vary in value from point to point of the state of reference).

12. Commentary on Pages 215–219. Solids Which Absorb Fluids. Elucidation of Some Mathematical Operations. In the final four pages of the section, viz., pp. 215–219, the general argument offers no difficulty and only a few comments need be made on the mathematical operations. Regarding the equations [463] and [464], we refer the reader to equations (38) of our exposition. If we are considering a state of hydrostatic stress, we know that

$$X_X = Y_Y = Z_Z = -p$$

and

$$Y_Z = Z_Y = Z_X = X_Z = X_Y = Y_X = 0.$$

Hence by (38)

$$X_{X'} = -A_{11}p, \qquad X_{Y'} = -A_{12}p,$$

$$X_{Z'} = -A_{13}p, \qquad Y_{Y'} = -A_{22}p, \qquad \text{etc.}$$

which constitute [463] of Gibbs.
Also

$$X_{X'}\delta a_{11} + X_{Y'}\delta a_{12} \ldots + Z_{Z'}\delta a_{33}$$

$$= -p(A_{11}\delta a_{11} + A_{12}\delta a_{12} \ldots + A_{33}\delta a_{33}).$$

As we have already seen on several occasions, the bracketed expression on the right hand side is δH, and of course H is the ratio of enlargement of volume, i.e., the volume of an element divided by its volume in the state of reference or $v_{V'}$. Thus we obtain [464].

The equations subsequent to [471] are obtained by the familiar device by means of which we obtain the ψ and ζ functions from the ϵ function. Thus since

$$d\epsilon_{V'} = t d\eta_{V'} + \Sigma\Sigma(X_{X'}\delta a_{11}) + \Sigma\mu_a d\Gamma_a',$$

we regard $\epsilon_{V'}$ as a function of $\eta_{V'}$, a_{11}, a_{12}, ... a_{33}, Γ_a', Γ_b', ... and the result just written embodies the equations

$$\frac{\partial \epsilon_{V'}}{\partial \eta_{V'}} = t, \quad \frac{\partial \epsilon_{V'}}{\partial a_{11}} = X_{X'}, \text{ etc.,} \quad \frac{\partial \epsilon_{V'}}{\partial \Gamma_a'} = \mu_a, \text{ etc.}$$

leading to [471] and other similar results. Also regarding $\psi_{V'} (= \epsilon_{V'} - t\eta_{V'})$ as a function of t, a_{11}, a_{12}, ... a_{33}, Γ_a', Γ_b', etc., we can write

$$\begin{aligned} d\psi_{V'} &= d(\epsilon_{V'} - t\eta_{V'}) \\ &= -\eta_{V'} dt + \Sigma\Sigma X_{X'} da_{11} + \Sigma \mu_a d\Gamma_a', \end{aligned}$$

and this is equivalent to the equations

$$\frac{\partial \psi_{V'}}{\partial t} = -\eta_{V'}, \quad \frac{\partial \psi_{V'}}{\partial a_{11}} = X_{X'}, \text{ etc.,} \quad \frac{\partial \psi_{V'}}{\partial \Gamma_a'} = \mu_a, \text{ etc.,}$$

which yield

$$\frac{\partial \eta_{V'}}{\partial a_{11}} = -\frac{\partial X_{X'}}{\partial t}$$

and similar results.

Also from either of these we obtain by repeated differentiation

$$\frac{\partial X_{X'}}{\partial \Gamma_a'} = \frac{\partial^2 \epsilon_{V'}}{\partial \Gamma_a' \, \partial a_{11}} = \frac{\partial \mu_a}{\partial a_{11}}$$

and so on, where $X_{X'}$, etc. and μ_a, etc. are regarded as functions of $\eta_{V'}$ (or t), a_{11}, a_{12}, ... a_{33}, Γ_a', Γ_b', etc.

We can also introduce a function $\phi_{V'}$ of t, a_{11}, a_{12}, ... a_{33}, μ_a, μ_b, etc. defined by

$$\phi_{V'} = \epsilon_{V'} - t\eta_{V'} - \mu_a \Gamma_a' - \mu_b \Gamma_b' - \text{etc.,}$$

whose differential satisfies the equation

$$d\phi_{V'} = -\eta_{V'} dt + \Sigma\Sigma X_{X'} da_{11} - \Sigma \Gamma_a' d\mu_a.$$

This will lead to the second group of [472].

The function $\zeta_{V'}$ of t, $X_{X'}$, $X_{Y'}$, ... $Z_{Z'}$, Γ_a', Γ_b', etc., defined by

$$\zeta_{V'} = \epsilon_{V'} - t\eta_{V'} - \Sigma\Sigma X_{X'}a_{11}$$

will give the second set of [473], and a function $\chi_{V'}$ of t, $X_{X'}$, $X_{Y'}$, ... $Z_{Z'}$, μ_a, μ_b, etc., defined by

$$\chi_{V'} = \epsilon_{V'} - t\eta_{V'} - \Sigma\Sigma X_{X'}a_{11} - \Sigma\mu_a\Gamma_a',$$

will yield the first group of [473].

The function $\epsilon_{V'}$ gives us the equation [471], viz.,

$$\frac{\partial t}{\partial a_{11}} = \frac{\partial X_{X'}}{\partial \eta_{V'}}$$

or

$$\frac{\partial t}{t\partial a_{11}} = \frac{\partial X_{X'}}{t\partial \eta_{V'}},$$

i.e.,

$$\frac{\partial \log t}{\partial a_{11}} = \frac{\partial X_{X'}}{\partial Q_{V'}},$$

and so on, which is the first group of [474].

The function $\psi_{V'}$ gives us

$$\frac{\partial \eta_{V'}}{\partial a_{11}} = -\frac{\partial X_{X'}}{\partial t},$$

i.e.,

$$\frac{\partial Q_{V'}}{\partial a_{11}} = -t\frac{\partial X_{X'}}{\partial t} = -\frac{\partial X_{X'}}{\partial \log t},$$

and so on, which is the second group of [475].

The function

$$\epsilon_{V'} - \Sigma\Sigma X_{X'}a_{11}$$

regarded as a function of $\eta_{V'}$, $X_{X'}$, $X_{Y'}$, ... $Z_{Z'}$, Γ_a', Γ_b', etc. will yield, when treated similarly, the second group of [474]; while the first group of [475] can be derived from the function $\zeta_{V'}$ in a similar manner.

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THE INFLUENCE OF SURFACES OF DISCONTINUITY UPON THE EQUILIBRIUM OF HETEROGENEOUS MASSES. THEORY OF CAPILLARITY

[*Gibbs, I, pp. 219–331; 331–337*]

JAMES RICE

I. Introductory Remarks

This part of Gibbs' work can be broadly divided into two portions; the first of these, and much the longer of the two, deals with surfaces of discontinuity between fluid masses, while the second consists of a brief treatment of liquid films and surfaces of discontinuity between solids and liquids. The first portion itself falls broadly into three parts, one of which, after formulating the general conditions of equilibrium in a surface phase between fluids, derives the famous "adsorption law" (a name not actually employed by Gibbs) and treats briefly the thermal and mechanical processes in such surface phases; another deals with the stability of surfaces of discontinuity; and the third part is concerned with the conditions relating to the formation of new phases and new surfaces of discontinuity. In addition, a few pages of the succeeding section on Electromotive Force are devoted to electrocapillarity, a commentary on which naturally belongs to this portion of the present volume.

1. The Surface of Discontinuity and the Dividing Surface

As Gibbs points out in the first paragraph of this section, the basic fact which necessitates a generalization of the results obtained in the preceding parts is the difference between the environment of a molecule situated well within a homogeneous mass and that of a molecule in the non-homogeneous region which separates two such homogeneous masses. In the subsequent pages he formulates in his customary careful and rigorous manner the fundamental differential equation for this region and gradually leads the reader to the abstract idea of a 'dividing surface" as a convenient *geometrical* fiction with which to represent the *physical* non-homogeneous region which has in reality extension in three dimensions, one however being very small. This region he frequently refers to as a "surface of discontinuity" but is careful to point out that the term does not imply that "the discontinuity is absolute," or that it "distinguishes any surface with mathematical precision." The term "dividing surface" does, however, refer to a surface in the strict geometrical sense and the reader is warned to keep this distinction well in mind. There is a certain latitude, as he will presently learn, in the precise position to be assigned to the dividing surface and in later developments of Gibbs' work this latitude has been the cause of some doubt concerning the validity of certain deductions.

In this way a certain part of the whole energy of the system is associated with this dividing surface. Now this part is not actually the energy situated in the non-homogeneous region or "surface of discontinuity," but is the excess of this energy over and above another quantity of energy whose amount depends on the precise location of the dividing surface. The matter is carefully dealt with by Gibbs (I, 223, 224), in equations [485] to [492]. Thus there is a certain latitude in the quantity of energy which is to be associated with the dividing surface, and this lack of precision in the value of this energy must not be lost sight of. A similar lack of precision accompanies the amounts of entropy and of the various components which are to be associated with the dividing surface, and whose actual values will in any given system depend to some extent on where we conceive the dividing surface to be situated. Gibbs denotes a physically small element of the dividing surface by s, and the quantities of energy, entropy, etc. associated with this element by ϵ^S, η^S, $m_1{}^S$, $m_2{}^S$, etc.

As is the case for any of the homogeneous phases, the variables which determine the state of such an element of the surface of discontinuity include the quantities s, η^S, $m_1{}^S$, $m_2{}^S$, etc., just referred to. The energy ϵ^S associated with the dividing surface is of course a function of these variables. (Actually Gibbs introduces the curvatures of the element of the surface as further variables, but disposes of them as of negligible importance, a point which we shall consider at a later stage, but shall ignore for the present.) The partial differential coefficient of ϵ^S with regard to η^S is of course the temperature of the discontinuous region, and those with regard to $m_1{}^S$, $m_2{}^S$, etc., are the chemical potentials of the various components in this region. In the first few pages of this section we are provided with a proof on exactly the same lines as that in Gibbs, I, 62 *et seq.* that the temperature and potentials in the discontinuous region are equal to those in the homogeneous masses separated by this region, provided of course that the usual condition is satisfied, viz., that the components in the surface are actual components of the homogeneous masses; if some of them are not, the usual inequalities hold. All this proceeds on familiar lines. There remains the partial differential coefficient of ϵ^S with regard to the variable s; this is denoted by σ. It is clearly the analogue of the partial differential coefficient of the energy of an ordinary homogeneous mass with respect to its volume, i.e., the negative pressure, $-p$, which exists in that phase. Equation [493] (with the last two terms omitted for the present as explained above) or equation [497] gives the formulation of the ideas just outlined. The paragraphs between equations [493] and [497] may well be omitted at this stage. The reader will then find that the succeeding two paragraphs lead in a direct and simple manner to the extremely important result expressed in equations [499] or [500].

2. *The Mechanical Significance of the Quantity Denoted by σ*

If the reader pauses to reflect he will observe that in the earlier portion of Gibbs' treatment the quantity $-p$ makes its appearance strictly as the partial differential coefficient of the energy with respect to the variable v. To be sure p has a mechanical significance which is always more or less consciously kept before us, but nevertheless in its original significance it is concerned with the quantity of energy which is passed into or out of a phase from or to its environment by reason of a simple volume change in the phase. Now it is to be observed that equation [500] opens up the possibility of giving a mechanical significance to σ, despite the purely formal introduction of it in [493] or [497]. It is well known that if a non-rigid membrane or a liquid film, such as a soap bubble, separates two regions in which there exist two different pressures p' and p'' then there exists a *surface tension* T uniform in all directions in the membrane or film, and moreover

$$p' - p'' = T(c_1 + c_2) ,$$

where c_1 and c_2 are the principal curvatures at any point of the membrane or film. The exact agreement of the form of this equation with [500] suggests a plausible mechanical interpretation for σ as a "superficial" or "surface" or "interfacial" tension. Actually in a converse fashion T, which is introduced as a tension in the membrane, can easily be given an interpretation in terms of energy. If the membrane, for instance, encloses a gas at pressure p' which receives (reversibly) an elementary amount of heat and expands by an amount δv, the increase of energy of the system, *gas and membrane,* is

$$t\,\delta\eta - p''\delta v ,$$

where p'' is the external pressure, since $p''\delta v$ is the amount of energy transferred by mechanical work from the internal gas-membrane system to the external gas system. Now, since

$$p'' = p' - T(c_1 + c_2) ,$$

it can be proved (the proof is a familiar one and will be found in the standard texts, being just a reversal of the steps in Gibbs' treatment between [499] and [500]) that

$$p''\delta v = p'\delta v - T\delta s ,$$

where s is the area of the whole membrane; and thus the increase of energy of the system, gas and membrane, is

$$t\delta\eta - p'\delta v + T\delta s.$$

The analogy between the quantity σ for an interface between two liquids or between a liquid and a gas, and the quantity T for a membrane in tension between two gases, is thus drawn once more from another standpoint. It is therefore quite natural for Gibbs at this point to say, as he does, that equation [499] or [500] "has evidently the same form as if a membrane without rigidity and having a tension σ, uniform in all directions, existed at the dividing surface," and thereupon to suggest the name "surface of tension" for a specially selected position of the dividing surface and the name "superficial tension" for σ. The cautious nature of Gibbs' statement might easily be overlooked by the reader. It clearly does not commit him to the view that the interface between two fluid masses must be regarded actually as a membrane in a state of tension. This idea is certainly a prevalent one, and the treatment of "surface tension" in many of the elementary texts of physics fosters it. So it may be of some service to the reader if a short discussion of this much debated point is inserted here. This will require us to enter into a more detailed consideration of the molecular structure of the fluid phases than actually occurs in the original, but that is hardly avoidable in any case in view of the developments of Gibbs' work by subsequent writers. In addition, later workers have availed themselves of the statistical calculations and results which are nowadays associated with molecular pictures of matter in order to give a deeper interpretation to some of Gibbs' results and to help to elucidate certain difficulties of the purely thermodynamical treatment. So it may prove serviceable to seize the opportunity at this point to give also a brief discussion of the fundamental statistical idea involved in such calculations.

II. Surface Tension

3. *Intrinsic Pressure and Cohesion in a Liquid*

The behavior of soap films, in which there may well be a strong lateral attraction between long-chain molecules such as those of the fatty acids, "anchored," as it were, side by side in the surfaces of the film (an attraction which may with some justification be really considered as a surface tension since it resembles a tension in an elastic membrane in most respects), gives a bias towards an explanation of the phenomena at the free surface of a simple liquid, or at the interface between two such liquids, in terms of the same concept. As already hinted, most elementary texts of physics deal with the "surface tensions" of liquids as if there did exist in their surfaces lateral pulls, tangential in direction, between the surface molecules, of an order of magnitude much greater than that exerted between these molecules and those immediately under them in the interior. At times one reads accounts of suspended drops of water which imply that the main body of water in the drop is contained in an "elastic" bag made of molecules which cohere together very powerfully like the molecules in a rubber sheet.

Now it is true that the *mathematical form* of the results deduced from such an assumption is precisely the same as that which can be deduced from a physically more real picture of the situation at a liquid surface; and it is also true that this assumption provides an easier mathematical route to these results then does the alternative hypothesis, which when worked out in detail involves rather troublesome analysis of a type first developed by Laplace. However, the course of that analysis and its outcome can be quite easily indicated without going into the purely analytical steps.

An analysis of the situation requires us first of all to be very careful concerning the interpretation of the word "pressure" in connection with a liquid. When we speak of the pressure of a gas we are thinking of the integral effect of the bombardment of the swiftly moving molecules on unit area of the enclosing vessel, or of the rate of transfer of normal momentum across unit area in the interior. The notion will be quite familiar to those who have some acquaintance with the kinetic theory of gases, and everyone recognizes that pressure *arising from weight* is usually an entirely evanescent quantity in a gas. Theoretically, of course, the pressure at a point in a gas increases as the point descends in level, but the difference of pressure between the top and bottom of an ordinary-sized vessel is negligible. On the other hand, the pressure in a liquid arising from the weight of a superincumbent column of liquid is in general the most important portion of the thrust on the enclosing vessel. Yet it only complicates the situation we are discussing to bring this in at all. It is best to conceive the liquid to be free from gravity, as Gibbs actually does in a great part of his treatise. We may, if we wish, consider it to be contained in a vessel which it touches everywhere, and which can be regarded as fitted with a piston so that a thrust can be applied if required,—a thrust which by Pascal's law is distributed at all parts of the surface in proportion to the size of each part, or is exerted normally across any conceptual dividing surface in the interior, again in proportion to its extent. Or we may think of the liquid as a spherical mass subject to the pressure of a surrounding gas and for the moment regard the sphere as so large that any small portion of the surface is practically plane. If now the pressure of the surrounding gas were zero the pressure would also vanish in the liquid. (Actually the pressure cannot be less than that of the saturated vapor.) The reader who has studied the earlier portion of Article K of this volume (pp. 395 to 429) will realize that this would be just a special case of an unstressed state of a body. Yet in the interior of the liquid there must be a relatively enormous pressure in the sense in which that word is used in connection with a gas; "kinetic" pressure we shall call it. In the liquid there exists a thermal motion of the molecules, and on account of the much larger density of the liquid the rate of transference of momentum across an interior conceptual surface is very great indeed. Clearly this internal kinetic pressure cannot be the quantity which is denoted by the symbol p in our equations; for that, as we have seen, would practically vanish when the stress in the liquid produced by the thrust of an external gas or piston in an enclosing vessel disappears. Of course at the surface there is the well known inward pull on each molecule in the layer whose thickness is equal to the radius of molecular attraction. This has the effect of turning inwards all but a small fraction of the molecules moving through this layer towards the surface, and in consequence the actual kinetic pressure at the surface is enormously reduced below the kinetic pressure which exists in the interior.

We may look at this matter from another standpoint, a purely static one. We can assume a molecular configuration practically unchanging in average conditions and imagine a plane to be drawn in the interior of the liquid. Across this plane there will be exerted repulsions between molecules in very close proximity to one another and attractions between molecules rather more separated. These ideas resemble somewhat those of Laplace who regarded the liquid as a continuum whose neighboring elements attract one another, this attraction tending to make the liquid contract; such contraction would be opposed by an internal pressure. These concepts of *cohesion* and *intrinsic pressure* are quite familiar. The molecular picture defines them a little more closely. The force between two molecules for distances greater than a certain critical amount is an attraction falling off in value very rapidly as the distance increases. At the critical distance, which must approximate in value to the size of a molecular diameter, the force is zero and changes to a repulsion when the distance apart is decreased; this repulsion must increase with very great rapidity as the distance apart is reduced below the critical separation. Van der Waals formulated these forces of cohesion and intrinsic pressure in his famous equation

$$p + \frac{a}{v^2} = \frac{Rt}{v - b},$$

for a/v^2 is nothing more than the cohesion varying directly as the square of the density, and $Rt/(v - b)$ is the intrinsic pressure varying inversely as the excess of the volume of the fluid above its irreducible minimum volume b. The symbol p represents the ordinary pressure with which we are concerned in the conditions of equilibrium. When p is small the cohesion and intrinsic pressure are nearly equal, which means that we have on the average a molecular configuration in which the repulsions and attractions across an internal plane nearly balance one another. The reader will recall in our discussion of the theory of elasticity (Article K) the warning that the stress-constituents X_x, X_y, etc. (which in the case of a fluid reduce to $-p$) are not to be confused with molecular attractions and repulsions, which may readily exist even in the "unstressed" state, when X_X, X_Y, etc., vanish. Just as the stress-constituents in the case of a strained solid arise from change of molecular configuration, i.e., strain, so the experimentally observable pressure p in a liquid arises from change in molecular repulsions and attractions due to the change in average molecular separation which we conceive to accompany compression.

4. Molecular Potential Energy in a Liquid

Having disposed of these considerations concerning pressure, which will be of service presently, we turn our attention to a treatment of the energy of a liquid from the point of view of molecular dynamics. We shall not, of course, go into the detailed mathematical analysis (which can be found by the reader in the works of Laplace or Gauss, or in accounts such as that of Gyemant in Geiger and Scheel's *Handbuch der Physik,* Vol. **7**, p. 345) but shall content ourselves with quoting certain important results. If we assume that there is a law of force between two molecules we can obtain in a familiar manner their mutual potential energy which we will represent by $\phi(r)$, where r is their distance apart. The magnitude of $\phi(r)$ increases as the molecules separate until r reaches a value at which the attractive force vanishes. For values of r greater than this the potential energy of the two molecules remains constant. In all expressions for potential energy there is an indefinite constant of integration and for purposes of calculation it is necessary to assign a definite value to this constant. In the present instance it is most convenient to choose the value of the integration constant in the function $\phi(r)$ to be such that the maximum value attained by $\phi(r)$ for sufficiently large separation of the molecules is zero. This makes the value of $\phi(r)$, for smaller values of r, negative, at all events until the critical separation is reached at which the attractive force is changed into a repulsion. There we have the minimum value of $\phi(r)$. (Of course, the *numerical* value of $\phi(r)$ will be greatest at this distance.) Any further decrease in r will produce an increase in $\phi(r)$, which will very quickly reach zero and even positive values owing to the enormous resistance to compression exhibited by liquids.

In terms of $\phi(r)$ it is easy to express the mutual potential energy of one molecule with respect to all the molecules within its sphere of action; but, of course, the result will vary according to the situation of the selected molecule. Suppose in the first instance that it is well within the general body of the liquid, so that a sphere around this molecule as center with a radius equal to the radius of molecular action, denoted by h, is completely filled with liquid. It is easy to see that the potential energy in question is represented by

$$4\pi n \int_l^h r^2 \phi(r) dr\,, \tag{1}$$

where n is the number of molecules per unit volume and l is the minimum distance between molecules, a distance which must approximate closely to the critical distance referred to above. Doubtless the integral form of this result should not be taken too seriously for purposes of actual calculation in view of our present-day knowledge of the properties of molecules, especially the fact that the radius of molecular action is not many times larger than a molecular diameter. But it will serve as a representative expression suitable for the purpose we have in mind, viz., the elucidation of the true nature of the "surface tension" of a simple liquid. Actually the numerical value of the expression (1) (we must bear in mind that it is an essentially negative quantity according to our conventions) is the amount by which the energy referred to is *less* than that for a molecule separated by relatively great distances from all others. It must also be noted that while this expression represents the potential energy of one molecule, this energy is nevertheless shared, as it were, with other molecules, so that when we wish to represent in a similar manner the potential energy of the group of molecules in unit volume we do not multiply the above expression by n but by $n/2$; otherwise we should be counting the energy of every pair of molecules twice. Thus the potential energy of the molecules in unit volume is

$$2\pi n^2 \int_l^h r^2 \phi(r) dr. \tag{2}$$

This expression is of course essentially negative by the convention stated above, which means that the *numerical value* of (2) is the amount by which the energy of these molecules is less than what it would be were they all widely separated from one another at the same temperature, i.e., in the gaseous state. If we now wish to obtain the potential energy of all the molecules in the body of liquid, we must not merely multiply the expression (2) by the volume. To do so would be to overlook the vital point that if a molecule lies in the layer of depth h at the surface, part of the sphere of molecular action lies outside the liquid and the expression (1) is not correct for the potential energy of this molecule. For such a molecule the contribution to expression (2) is *numerically* smaller since n is zero* for certain elements of the spherical volume of radius h surrounding it; but as $\phi(r)$ is negative for the values of r considered, the contribution of this molecule to the total potential energy is greater than for a molecule in the interior of the liquid. In short, if a body of liquid is divided into two portions which are then separated from one another against mutual attraction we know that the potential energy of the whole is increased. This increase is made up of the larger contributions of those molecules which lie near to the two new surfaces created by the division. This increase can be calculated in terms of $\phi(r)$ and we can thus obtain an expression which represents the "surface energy," meaning by that the extra energy associated with the molecules in the surface layer of thickness h over and above that which would be associated with them if they were all in the interior of the liquid mass. This is not the place to enter into the analytical details, but it can be shown that the whole potential energy of the body of liquid can be written in the form

$$\rho V + \sigma A ,$$

where V and A are the volume and superficial area of the mass;

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* Actually it is the concentration of the vapor or gas phase, rather than zero.

ρ is the expression (2) and σ is the expression

$$-\frac{\pi n^2}{2}\int_l^h r^3\phi(r)dr^*. \tag{3}$$

(Once more, since the definite integral in (3) is essentially negative, σ itself is essentially positive.) The expression (3) represents the potential energy per unit area of surface. This is not the whole energy of the surface since in that we must also include the kinetic energy of the molecules in the surface layer. We have here a mechanical interpretation of the well-known division of the total surface energy into the surface "free energy" σ, and the "bound energy" $-t d\sigma/dt$.

5. *An Alternative Method of Treatment*

There is another method of approaching this question of surface energy which leads to the same result. In the interior of a liquid mass there is on a given molecule no force permanently acting in a given direction. As the molecule changes its relative position and suffers many more encounters with other molecules than it would meet in a gas in the same time, the attractions and repulsions of its neighbors on it change in a fortuitous fashion. At the surface of a liquid, within the layer of thickness h, there is an inward normal resultant force on a molecule which increases in value as the molecule approaches the surface. Also in a layer of the vapor outside the surface of the liquid this field of force also exists, reaching the value zero when the molecule is at a distance h from the surface. A molecule in such a situation possesses potential energy, just like a body raised above the ground against gravity. Just as a body under gravity tends to move downwards, so molecules in the surface tend to "fall inwards" towards the interior and so reduce the extent of the surface, thus producing the illusion of a surface contracting "under tension." But of course the truth is that the effective force on a molecule in the surface layer is not parallel to the surface but normal to it. As stated above, it is by reason of this that the enormous kinetic pressure in the interior (the intrinsic pressure) never manifests itself to our senses or our measuring instruments. Only a small fraction of the molecules, whose kinetic energy is sufficiently above the average and whose direction of motion is sufficiently near to the direction of the outward normal, will manage to effect their escape and impinge on an enclosing solid wall or enter into a vapor phase. Thus it is that, apart from artificially produced thrusts on the surface of the liquid mass and the effects of gravity, the observed pressure of the liquid is just the saturated vapor pressure.

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* In arriving at (3) certain assumptions are made about the behavior of $\phi(r)$ and certain functions derived from it at the lower limit l of r. This, however, concerns mathematical details and does not concern physical interpretation.

This picture of the surface conditions enables us to make a calculation of the surface potential energy in a manner alternative to that suggested earlier. The basic idea of it is just the same as that employed in calculating the potential energy of a body raised above the ground; perhaps the potential energy of a wall of given height is a better analogy. The details are again too troublesome to reproduce here, but once more we reach the same result as before for this energy per unit area of surface, viz., the expression (3).

This second method of analyzing the situation also enables us to obtain a formula for the "cohesion," i.e., the amount by which the intrinsic pressure of the liquid exceeds the observed pressure. It can be shown that the attraction of the interior liquid on all the molecules contained in the amount of surface layer which lies under unit area of surface is

$$-2\pi n^2 \int_l^h r^2 \phi(r) dr. \tag{4}$$

(This happens to be expression (2) with the sign reversed.) This is the well-known result of Laplace, and this expression (4) for the "cohesion" is usually denoted by the letter K. It is, of course, as well to remember that this expression, like the previous results, is derived on the assumption of a liquid so fine-grained in structure as to be practically continuous, and therefore these expressions can only be regarded as approximate representations of the proper formulae in the case of an actual liquid. This, however, does not invalidate the general tenor of the argument. The expression (4) for K represents the van der Waals' cohesion a/v^2. If the constant a is reckoned for unit mass of the liquid it is easy to see that

$$a = -\frac{2\pi}{m^2}\int_l^h r^2\phi(r)dr\,,$$

where m is the mass of a molecule.

III. The Quasi-Tensional Effects at a Curved Surface

6. *Modification of the Previous Analysis*

Hitherto we have regarded the surface of a liquid mass as plane. When we consider the situation in a surface layer at a curved surface we have to modify the calculation of the inward attraction on this layer. In the same broad manner as before we can indicate the modification and thereupon it will be clear how it comes about that the quantity represented by σ, which is manifestly an energy per unit area, appears to take on the rôle of a surface tension, i.e., a force *per unit length*. (It is, of course, obvious that energy/area and force/length have the same physical dimensions.) To make this clear we shall have to indicate in a little more detail how the calculation which leads to (4) is effected. In Figure 1, A is a point in the surface (supposed plane) and C a point at the distance h below. If P represents the position of a molecule in the layer, we consider another point B such that $AP = PB$; it is then clear that the layer of liquid between the surface of the liquid mass and the parallel surface through B produces no resultant force on the molecule at P. Thus the inward attraction on P will arise from the layer of liquid between the surfaces through B and C, and a little thought will show how this attraction increases as P approaches A. This argument is made use of in the calculation of the entire force on all the molecules lying between the surface through A and that through C,—a calculation which, as stated, leads to (4). Supposing, however, that the surface of the liquid were spherical and convex, and that we were proceeding as before to determine the attraction inwards on a molecule situated at P; we realize at once that the layer of liquid near the surface which has no resultant effect on the molecule is not bounded by a plane surface through B but by a concave one having the same curvature as the surface of the liquid mass. The net result of this will be that the inward attraction on the molecule will be greater than for a similar situation beneath a plane surface, since in the latter case we determine the effect of the molecules under the plane surface DBE (see Figure 2), whereas in the former we include the effect of the molecules between the surfaces DBE and FBG as well When the analysis

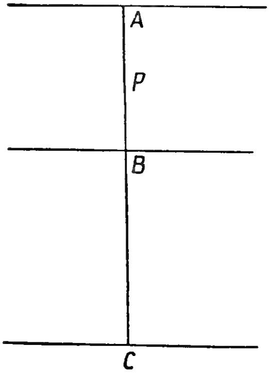

FIG. 1

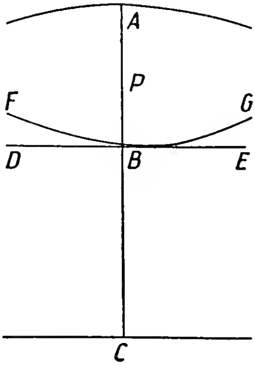

FIG. 2

is carried out it yields the result that the inward attraction on a small prism of the liquid at the surface, whose depth is h and whose sectional area is δs, is equal to

$$\delta s\left\{-2\pi n^2\int_l^h r^2\phi(r)dr - \frac{\pi n^2}{R}\int_l^h r^3\phi(r)dr\right\},$$

where R is the radius of curvature of the spherical surface. A reference to (3) and (4) shows that this is just

$$\delta s\left\{K + \frac{2\sigma}{R}\right\}. \tag{5}$$

Were the surface of the liquid mass concave, we could show in a similar manner that the attraction on a molecule situated at P would be less than for a plane surface and that the result for the total attraction on the prism would work out to be

$$\delta s\left\{K - \frac{2\sigma}{R}\right\}. \tag{6}$$

The analysis is due to Laplace, and it is customary to denote the quantity 2σ by the letter H. (See, for example, Freundlich's *Colloid and Capillary Chemistry,* English translation of the third German edition, pp. 7–9, where K is called the internal pressure, an unfortunate term since K is a *cohesional attraction* and not a pressure, and H/R is referred to as a surface pressure, another unfortunate name for what is really an *additional* cohesion.)

7. *Interpretation of σ as a Tension*

We can now use this material to elucidate the apparent rôle of σ in this connection. In the first place, if we consider a plane surface we have the result

$$P_0 - K = p_0, \tag{7}$$

where P_0 stands for the intrinsic pressure within a (weightless) liquid bounded by a plane surface,* and p_0 stands for the external pressure on its surface which arises from its saturated vapor (with the possible addition of effects arising from artificial thrusts). Actually, even for a liquid under gravity, we can regard P_0 as the intrinsic pressure just within the horizontal free surface. As the depth increases, the intrinsic pressure, just like the usual "hydrostatic pressure", will increase by the amount $g\rho z$, where ρ is the density of the liquid and z the depth. Now P_0 arises from the momentum of the thermal motion of the molecules of the liquid, and $P_0 - K$ represents this kinetic pressure enormously reduced by the cohesion on the surface layer. We might therefore call $P_0 - K$ the internal pressure of the liquid at the surface, but care will have to be taken to avoid any confusion between this use of the term "internal pressure" and the use of it by Freundlich and others (erroneously in the writer's opinion) to refer to the cohesion K.* On the other hand p_0 is the external pressure on the surface of the liquid and is the pressure actually measured by a manometer; so that the result for a plane surface simply states that the external and internal pressures at the surface are equal. Turning now to a spherical surface of radius R (convex to the exterior), the expression (5) yields the result

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* I.e., by a spherical surface of very large radius.

$$P - \left(K + \frac{2\sigma}{R}\right) = p\,, \tag{8}$$

where P is the intrinsic pressure inside the liquid mass (at any point if the liquid is weightless, or at the free surface if gravity is supposed to act) and p is the external (observable) pressure on the surface. As before, we may call $P - K$ the internal pressure of the liquid at its surface, and denoting this by p' we have

$$p' - p = \frac{2\sigma}{R}\,. \tag{9}$$

Now this result is identical in form with that which connects the gas pressure inside a membrane or liquid film and that external to it. This formal identity has led to the use of the term "surface tension" for the quantity denoted by σ, with unfortunate results for the real understanding of certain phenomena by students reading elementary accounts of capillary rise, for example. In consequence vague notions are prevalent that in some way a tight skin of water holds up the elevated column in the capillary tube and "pins it" to the inner wall, or, on the other hand, that a tight skin of mercury holds the mercury in a capillary tube down below the general level in the vessel outside. In the case of a spherical membrane under tension enclosing one body of gas and surrounded by another, both pressures are available for observation, the inside as well as the outside. In the present instance the intrinsic pressure of the liquid is not open to observation, nor its cohesion; but we can infer from the result (9) that the internal pressure just within a spherical mass of liquid, subject to a definite external pressure, is greater than it would be under a plane surface, subject to the same external pressure, by the amount $2\sigma/R$. In short the liquid in the sphere is a little more compressed than that under the plane surface, but this extra compression is not due to a "surface membrane" in tension, but to a small change in the inward attraction on the membrane due to the curvature. Indeed the elevations and depressions observed in capillary tubes are easily seen to arise indirectly from this cause. In the first instance, the curvature at the surface of water in a capillary tube dipping into a beaker of this liquid is caused by the strong molecular attraction of glass on water as compared to the attraction between the molecules of water (water "wets" glass and adheres powerfully to it). This concave curvature can only exist if the internal pressure just at the surface is less than the external pressure; this external pressure is practically the same as exists on the plane surface of the water in the beaker. Thus the internal pressure just under the curved surface in the tube is less than that under the plane surface in the beaker, and this cannot be so unless the level in the tube is higher than in the beaker; in short the column in the capillary tube is *pushed up*, not pulled up. For a liquid like mercury which adheres scarcely at all to glass, the absence of molecular attraction by the glass necessitates a convex curvature in the capillary tube, and a similar argument demonstrates that the mercury must be pushed down in the tube, in order to preserve conditions of hydrostatic equilibrium.

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* Or we might use the old-fashioned phrase "vapor-tension" for $P_0 - K$, as distinct from "vapor-pressure" the term for p_0.

The writer feels that there exists so much misconception concerning the surface tension of liquids that the preceding elementary account may not be out of place at the outset of a commentary on a portion of Gibbs' work which is so vitally concerned with the concept of surface energy, with which the term "surface tension" has come to be practically synonymous. Before proceeding, it may be desirable to take this opportunity to clear up a misconception about another matter which experience shows to occur often in this connection. Outside a spherical mass of liquid the vapor pressure is *less* than the internal pressure just inside the surface. It is quite easy, as the writer knows from teaching experience, for the unwary student to pick up the notion that the saturated vapor pressure outside a liquid with a convex surface is therefore less than that outside a plane surface; but, of course, the very reverse of this is true. The capillary tube phenomena actually demonstrate this, as well as the complementary fact that the saturated vapor pressure above a concave surface is less than that above a plane surface. The chapter on the vapor state in any good text of physics contains the necessary details on this point. Moreover, the matter can be argued out correctly from statistical considerations. In any case the equations (7) and (8) show that

$$P - p > P_0 - p_0,$$

but unless we had some definite prior information concerning the equality or inequality of P and P_0 we could draw no inference from this as to the relation of p to p_0. Actually, as stated just above, capillary experiments or statistical arguments demonstrate that $p > p_0$, and so we can infer from this fact that $P > P_0$ also.

IV. Statistical Considerations

8. *The Finite Size of Molecules*

While the foregoing analysis is very instructive in giving some insight into the true nature of the conditions at the surface of a liquid, it is limited by the fact that implicitly it regards the liquid as divisible into elements infinitesimally small compared to the range of molecular attraction, and this is not the case in actual fluids. However, molecules although not mathematically infinitesimal in size are so small that great numbers of them exist even in any "physically small" volume of a gas. By "physically small" we mean small in so far as our capacity to deal with it experimentally is concerned. Under such conditions we can apply certain well-known statistical results which will prove of service to us later when we shall endeavor to supplement the thermodynamical arguments of Gibbs' treatment by considerations based on molecular structure.

The previous discussion introduced us to an expression which represents the potential energy of one molecule with respect to its surrounding neighbors. It is given in (1), and ostensibly it is proportional to n, the numerical concentration of the molecules. We have already noted the hypothesis of infinite subdivision of the fluid on which this is based. But even if we waive that difficulty we must draw attention to the fact that the factor multiplying n is a function of the lower limit of the integral, viz., l. Now this limit is by no means so definite as the upper limit. Undoubtedly, if the concentration is not too great, we may take it to be a fixed quantity so that the expression in (1) may be regarded as varying directly with n; and as we have seen it then supplies the theoretical basis for van der Waals' cohesion term. But as the concentration increases, or as the temperature rises so that molecular impacts are on the average more violent and penetration of molecule into molecule more pronounced, the quantity l itself will become a function of concentration and temperature. Thus the linearity in n of the function expressing this mutual potential energy disappears at sufficiently high concentrations. We shall still require this conception of the potential energy of one molecule with respect to the others or, to put the definition in another form, the change of energy produced by introducing one more molecule into the system, and we shall consider it as some function of concentration and temperature. Of course, one part of this change will be the average kinetic energy of one molecule; with that we are not seriously concerned; it is the average potential energy of a molecule with regard to all the others with which we wish to deal, and we shall represent it as a function of the concentration, say $\theta(n)$. As stated, if n is sufficiently small $\theta(n)$ is simply a multiple of n and is, according to our conventions, negative, approaching the value zero as n approaches zero. But at sufficiently large concentrations $\theta(n)$ will reach a minimum (negative) value and as the effect of intermolecular repulsive force begins to make itself more marked in the great incompressibility of the fluid, $\theta(n)$ will increase in value with further increase in the value of n and must be considered as theoretically capable of reaching any (positive) value, however large, unless density is to grow without limit.

9. *Distribution of Molecules in Two Contiguous Phases*

Now suppose that we have two phases of the fluid in a system, represented by suffixes 1 and 2. The gain in energy of a molecule when it passes from the second phase to the first is $\theta(n_1) - \theta(n_2)$. (We are assuming that the average kinetic energy of a molecule is the same in each phase.) It is a well-known result familiar to those acquainted with the elements of statistical mechanics that the concentrations in the two phases are related by the equation

$$\frac{n_1}{n_2} = \exp\left\{-\frac{\theta(n_1) - \theta(n_2)}{kt}\right\}, \tag{10}$$

where k is the "gas constant per molecule," i.e., the quotient of the gas constant for any quantity of gas divided by the number of molecules in this quantity.*

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* For a gram-molecule, $R = 8.4 \times 10^7$; $N = 6.03 \times 10^{23}$; so $k = R/N = 1.36 \times 10^{-16}$. Exp$(x)$ is the exponential function of x, viz., the limit of the infinite convergent series

$$1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots,$$

$$\exp(x) = e^x,$$

where e is the Napierian base of logarithms.

By taking logarithms we can write this in the form

$$\log n_1 + \frac{\theta(n_1)}{kt} = \log n_2 + \frac{\theta(n_2)}{kt}$$

or, if we represent the gram-molecular gas constant by R and the number of molecules in a gram-molecule by N, we can write it thus:

$$Rt \log n_1 + N\theta(n_1) = Rt \log n_2 + N\theta(n_2). \tag{11}$$

If the first phase is a vapor, so that $\theta(n_1)$ approaches zero, the expression on the left-hand side approaches $Rt \log n_1$.

Now, as is well known, the chemical potential of a gram-molecule of a dissolved substance, provided its concentration is small, is given by $Rt \log n_1$, where n_1 is the concentration. In seeking to discover how this formula must be generalized so as to embrace more concentrated states, statistical as well as thermodynamical argument may easily prove of service, and the equation (11) gives a hint of a possible line of attack. Equation (10) shows that the function

$$Rt \log n + N\theta(n)$$

is the same in both phases of the fluid. When we remember that the chemical potential of a given component is the same in all phases in equilibrium, and compare $Rt \log n$ with the formula for the chemical potential of a weakly concentrated component, we may well consider that the full expression just written might prove to be the pattern for a formula for the chemical potential under other conditions. We shall return to this point in the commentary.

In conclusion, we may point out a phenomenon at the surface of a liquid which bears some resemblance to adsorption, and is explained by statistical considerations. When we were treating the field of force which exists at the surface separating liquid and vapor it was mentioned that the field exists in a layer of the vapor as well as in a layer of the liquid extending in both cases as far as the radius of molecular action. Now, just as the density of our atmosphere is greater the nearer we are to the ground, so this field in the vapor will tend to retain molecules in this layer in greater number than exist in an equal volume elsewhere in the vapor; so that at the surface there is an excess concentration in the vapor phase. Furthermore this "adsorption" is accompanied by a decrease of the surface energy; for the reader will recall the fact that any concentration of molecules near the surface of the liquid tends to reduce the total potential energy, since the nearer one molecule is to another, outside the distance where repulsion begins, the smaller their mutual potential energy. Again there is an analogy with the mechanical conditions in the atmosphere, since any aggregation of molecules of air in the lower levels produces a diminution of potential energy as compared with a state of affairs in which the molecules are more uniformly distributed in the atmosphere. Indeed, when one is endeavoring to interpret thermodynamic phenomena in terms of mechanical laws, we may expect to find that any occurrence in which free energy tends to decrease is to be explained by the mechanical fact that, in the passage of an isolated dynamical system to a state of equilibrium, potential energy always tends to a minimum.

V. The Dividing Surface

10. Criterion for Locating the Surface of Tension

We now return to the text of the treatise and consider one of the most troublesome features of the earlier pages of this section, viz., the location of the abstract dividing surface which in the course of the reasoning replaces the non-homogeneous film or region of discontinuity. The argument of Gibbs (I, 225–228) leads to a criterion based on theoretical grounds for locating this surface in a precise fashion; yet, as will appear, it is one which gives way in practice to other methods of placing the surface more suitable for comparing the deductions from the adsorption equation [508] with the results of experiments. Nevertheless, as there are one or two points in the argument which may require elucidation, we shall devote some consideration to it. Fig. 3 will help to illustrate Gibbs' reasoning. He chooses first an arbitrary position for the dividing surface which he calls S. In the figure, K represents the closed surface which cuts the surface S and includes part of the homogeneous masses on each side; the portion of K which cuts S and is within the non-homogeneous region is generated by a moving normal to S; the remaining parts of K in the homogeneous masses may be drawn in any convenient fashion. The portion of S referred to by the letter **s** (in Clarendon type) is indicated by AB in the figure, and its area is given by the italic s. CD and EF indicate portions of the other two surfaces mentioned at the top of page 220. The parts referred to in Gibbs' text by the letters, M, M', M'' are also indicated in the figure. In the succeeding paragraph the difficulty of defining the exact amounts of energy to be attributed to masses separated from one another by a surface where a discontinuity exists is touched on, but, in view of what has already been said above, this matter will probably be easily grasped by the reader, and in the immediately following pages the development follows that of the earlier parts of Gibbs' treatise, i.e., on pages 65 *et seq.* Great care is required when we reach page 224 to observe just what Gibbs means by the energy and entropy of the dividing surface S, and the superficial densities of these and of the several components. The definitions and arguments are quite clear, and the figure

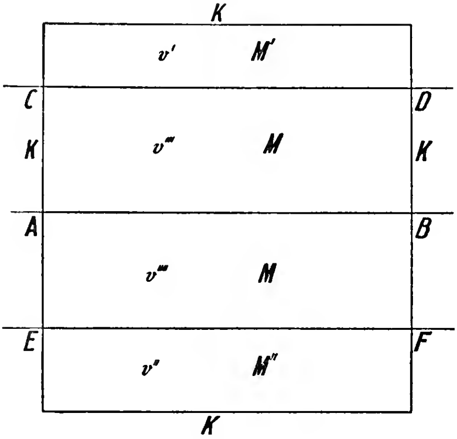

FIG. 3

may help to visualize the situation; nevertheless it cannot be too strongly emphasized here in view of the references later to experimental work that ϵ^S, η^S, $m_1{}^S$, etc. do not refer to the actual quantities of energy, entropy, etc. in the discontinuous region, but to the *excesses of these* over those quantities which would be present under the arrangement postulated in the text with reference to the surface S. The actual quantities present are of course precisely determined by the physical circumstances of the system; the quantities ϵ^S, η^S, $m_1{}^S$, etc. are, however, partly determined by the position chosen for the surface S. (This is a point more fully elaborated later by Gibbs on page 234.) That being so, there is something arbitrary about their values unless we can select a position for S by means of some definite physical criterion. Such a criterion Gibbs suggests and deals with in pages 225–229. He calls this special position the *surface of tension.*

11. *An Amplification of Gibbs' Treatment*

The criterion is based on the formal development of the fundamental differential equation for the dividing surface regarded as if it were a homogeneous phase of the whole system. As usual the energy ϵ^S of the portion s of the surface is regarded as a function of the variables, η^S, $m_1{}^S$, $m_2{}^S$, etc. Among these variables must of course be included the area s of s; but in addition there exist two other geometric quantities; these measure the curvature of s (regarded as sufficiently small to be of uniform curvature throughout), viz., the principal curvatures c_1 and c_2. It is a possibility that a variation of the curvature of s, which would obviously involve an alteration in form of the actual region of discontinuity, would cause a change in the value of ϵ^S and in consequence we must regard ϵ^S as dependent to some extent on c_1 and c_2. The partial differential coefficients $\partial\epsilon^S/\partial c_1$ and $\partial\epsilon^S/\partial c_2$ are denoted by C_1 and C_2. Now we know that ϵ^S is dependent in value on the position which we assign to s; also it appears that the values of the differential coefficients just mentioned depend to some extent on the position and form of s. Gibbs chooses that position of s, which makes

$$\frac{\partial \epsilon^S}{\partial c_1} + \frac{\partial \epsilon^S}{\partial c_2}$$

equal to zero, to be coincident with the surface of tension. The proof that such a position can be found and the reasons for choosing it are expounded at length. In view of the fact that Gibbs takes S to be composed of parts which are approximately plane and which are supposed in the course of the proof to be deformed into spherical forms of small curvature, we may as well introduce that simplification into the argument at once and assume that $c_1 = c_2$ so that $C_1 = C_2$, and we have then to show that we can locate **s** in such a way that

$$\frac{\partial \epsilon^S}{\partial c} = 0\,,$$

where c is the common value of c_1 and c_2.

Let $CDEF$ in Fig. 4 represent the portion of the region of discontinuity, and suppose AB represents an arbitrarily assigned position of **s** so that $EA = FB = x$. We shall represent the thickness of the film EC by ζ. We now suppose that a deformation to a spherical form indicated by the diagram with accented letters is produced. This means that c varies from zero to $1/R$, where R is the radius of the sphere of which $A'B'$ is a portion; i.e., $\delta c = 1/R$. We also suppose that s does not vary in magnitude; i.e., that the area of the spherical cap indicated by $A'B'$ is equal to the area of the plane portion indicated by AB; nor is there to be any variation of the other variables η^S, $m_1{}^S$, $m_2{}^S$, etc. Hence, by [493],

$$\delta\epsilon^S = 2C\delta c = 2\,\frac{C}{R}.$$

But the only possible reason for which ϵ^S will vary under these circumstances is the fact that the *volume* of the element of film indicated by $C'D'E'F'$ is different from that of the element $CDEF$. In short one must remember that σ, though called a surface energy, is strictly an energy located in the film with a volume density σ/ζ. Consequently $\delta\epsilon^S$ will be equal to the product of σ/ζ and the difference in the volumes of the elements just mentioned. On working this out we shall be able to obtain some information concerning the order of magnitude of C and justify the statements which Gibbs makes on this point in the paragraph beginning at the middle of page 227. It is true he begins the paragraph with the words: "Now we may easily convince ourselves by equation [493] . . ." but the reader may well be pardoned if he doubts whether conviction is so readily obtained. Since the solid angle subtended by $A'B'$ at the centre of the sphere is s/R^2, it is proved by well-known propositions in solid geometry that the volume of the spherical film $C'D'E'F'$ is

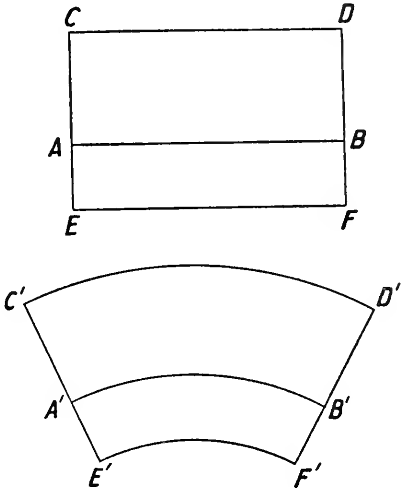

FIG. 4

$$\frac{1}{3}\frac{s}{R^2}\{(R+\zeta-x)^3-(R-x)^3\},$$

since $R-x$ is the radius of the sphere on which $E'F'$ lies and $R+\zeta-x$ the radius of that on which $C'D'$ lies, R being the radius of $A'B'$. This volume is equal to

$$\frac{1}{3}\frac{s}{R^2}\{3R^2(\zeta - x) + 3R(\zeta - x)^2 + (\zeta - x)^3 + 3R^2x - 3Rx^2 + x^3\}$$

$$= s\zeta + \frac{s}{R}(\zeta^2 - 2\zeta x),$$

neglecting the remaining terms which involve squares and products of ζ/R and x/R. Hence the difference of the volume elements is

$$\frac{s}{R}(\zeta^2 - 2\zeta x),$$

and so the value for $\delta\epsilon^S$ calculated as suggested above is equal to

$$\frac{s}{R}(\zeta^2 - 2\zeta x)\frac{\sigma}{\zeta}$$

$$= \frac{\sigma s}{R}(\zeta - 2x).$$

This is the same as $2C\delta c$, i.e., $2C/R$. Hence we find that

$$C = \tfrac{1}{2}\sigma s(\zeta - 2x).$$

From this equation it is clear that C can have positive or negative values according as x is less or greater than $\zeta/2$. C is zero if $x = \zeta/2$, i.e., if the dividing surface is midway in the film. Also if C' is the value of C when $x = x'$, and C'' its value when $x = x''$, these being in fact the values of C for two positions of the dividing surface separated by λ, where $\lambda = x' - x''$, we have

$$2(C'' - C') = 2\sigma s(x' - x'') = 2\sigma s\lambda.$$

In this way we confirm the results obtained by Gibbs on page 227. These results show that we can choose in any general case a position for s which gets rid of the awkward terms $C_1\delta c_1 + C_2\delta c_2$ in [493]; our sole object in presenting an alternative method of derivation has been to show the physical basis for introducing these terms at all. It may also help the reader to a further insight into the argument presented by Gibbs on page 226. Before leaving this topic, however, it may be as well to enjoin on the reader the necessity of keeping Gibbs' own caution in mind that in strict theory it is only for this specially chosen position of the dividing surface that the equation [500] is valid, and that only to it may the term surface of tension be correctly applied.

VI. The Adsorption Equation

12. Linear Functional Relations in Volume Phases

Let us revert for a moment to the substance of pages 85–87 of Gibbs, which leads to the equation [93]. Divested as far as possible of the mathematical dressing, the simple physical fact on which it rests is this. We are considering two homogeneous masses identical in constitution and differing only in the volume which they occupy. If the volume of the first mass is r times that of the second, then the amount of a given constituent in the first is r times that of the same constituent in the second; also the energy and entropy of the first are respectively r times the energy and entropy of the second. Hence, when we express ϵ as a function of the variables η, v, m_1, m_2, $\ldots$ m_n, writing for example,

$$\epsilon = \phi(\eta, v, m_1, m_2, \ldots m_n),$$

we know that

$$\phi(r\eta, rv, rm_1, rm_2, \ldots rm_n) = r\phi(\eta, v, m_1, m_2, \ldots m_n).$$

In other words, the function ϕ is a homogeneous function of the first degree in its variables.* There is a well-known theorem of

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* It should be observed that this does not of necessity mean a *linear* function. Thus $ax + by + cz$ is a linear function of the variables x, y, z; but

$$\frac{ax^2 + by^2 + cz^2}{lx + my + nz}$$

is not. Yet both are homogeneous functions of the first degree; for if x, y, z are all altered in the same ratio, the values of these functions are also altered in the same ratio.

the calculus due to Euler, which states that if $\psi(x, y, z, \ldots)$ is a homogeneous function of the qth degree in its variables then

$$x\frac{\partial\psi}{\partial x} + y\frac{\partial\psi}{\partial y} + z\frac{\partial\psi}{\partial z} + \ldots = q\psi.$$

As a special case of this we see that

$$\eta\frac{\partial\phi}{\partial\eta} + v\frac{\partial\phi}{\partial v} + m_1\frac{\partial\phi}{\partial m_1} + m_2\frac{\partial\phi}{\partial m_2} \ldots + m_n\frac{\partial\phi}{\partial m_n} = \phi.$$

But by the fundamental differential equation [86] which expresses the conditions of equilibrium

$$\frac{\partial\phi}{\partial\eta} = t; \quad \frac{\partial\phi}{\partial v} = -p; \quad \frac{\partial\phi}{\partial m_1} = \mu_1, \quad \text{etc.}$$

Hence

$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n,$$

which is equation [93].

13. *Linear Functional Relations in Surface Phases*

Precisely similar arguments justify equation [502], since we assume as an obvious physical fact that if we consider two surfaces of discontinuity of exactly similar constitution then the entropy, energy, and amounts of the several components in each would be proportional to the superficial extent of each. Since ϵ^S is homogeneous of the first degree in the variables η^S, s, $m_1{}^S$, $m_2{}^S$, etc., it follows that the partial differential coefficients of the function $\phi(\eta^S, s, m_1{}^S, m_2{}^S, \ldots)$ of these variables, which is equal to ϵ^S, with regard to the variables are individually also homogeneous functions of the variables of degree zero, i.e., they are functions of the ratios of these variables. But by [497]

$$t = \frac{\partial\phi}{\partial\eta^S}, \quad \sigma = \frac{\partial\phi}{\partial s}, \quad \mu_1 = \frac{\partial\phi}{\partial m_1{}^S}, \quad \text{etc.} \qquad (12)$$

Hence the $n + 2$ quantities t, σ, μ_1, μ_2, $\ldots$ are functions of the $n + 1$ variables $\eta_S = \eta^S/s$, $\Gamma_1 = m_1{}^S/s$, $\Gamma_2 = m_2{}^S/s$, etc. By means of the $n + 1$ equations which express t, μ_1, μ_2, etc. as functions of the $n + 1$ quantities η_S, Γ_1, Γ_2, etc., we can theoretically express η_S, Γ_1, Γ_2, etc. as functions of t, μ_1, μ_2, etc. In consequence σ, which is also, as we have just seen, a function of the former set of $n + 1$ quantities, can be expressed as a function of the second set, viz., t, μ_1, μ_2, etc. This functional relation between σ and the new variables t, μ_1, μ_2, etc. is referred to by Gibbs as "a fundamental equation for the surface of discontinuity." Now the values of the potentials μ_1, μ_2, etc., are themselves determined by the constitution of the phases or homogeneous masses separated by the surface of discontinuity; so we see that σ is itself ultimately dependent on the constitution of the adjacent phases and the temperature (unless any of the potentials relate to substances only to be found at the surface). Furthermore, as we know, the pressures p' and p'' in these phases are also determined by the temperature and the potentials. Since by equation [500]

$$c_1 + c_2 = \frac{p' - p''}{\sigma},$$

it follows that the curvature of the dividing surface is also dependent on the temperature and the constitution of the phases separated by it.

14. Derivation of Gibbs' Adsorption Equation

Suppose the constitution of the phases suffers a change so that a new equilibrium is established at a temperature $t + dt$, with new values of the potentials in the phases equal to $\mu_1 + d\mu_1$, $\mu_2 + d\mu_2$, etc. This will involve changes in the surface energy, entropy and masses to values $\epsilon^S + d\epsilon^S$, $\eta^S + d\eta^S$, $m_1{}^S + dm_1{}^S$, $m_2{}^S + dm_2{}^S$, etc., and the surface tension will alter to $\sigma + d\sigma$. The equation [502] still holds for this neighboring state of equilibrium, so that

$$\begin{aligned}\epsilon^S + d\epsilon^S = (t + dt)\ (\eta^S + d\eta^S) + (\sigma + d\sigma)\ (s + ds) \\ + (\mu_1 + d\mu_1)\ (m_1{}^S + dm_1{}^S) + \text{etc.}\end{aligned}$$

or, neglecting quantities of the second order,

$$d\epsilon^S = td\eta^S + \eta^S dt + \sigma ds + sd\sigma + \mu_1 dm_1 + m_1 d\mu_1 + \text{etc.}$$

But since ϵ^S is equal to a function $\phi(\eta^S, s, m_1{}^S, m_2{}^S, \ldots)$ of $\eta^S, s, m_1{}^S, m_2{}^S$, etc.,

$$\begin{aligned} d\epsilon^S &= \frac{\partial\phi}{\partial\eta^S} d\eta^S + \frac{\partial\phi}{\partial s} ds + \frac{\partial\phi}{\partial m_1{}^S} dm_1{}^S + \frac{\partial\phi}{\partial m_2{}^S} dm_2{}^S + \ldots \\ &= td\eta^S + \sigma ds + \mu_1\, dm_1{}^S + \mu_2\, dm_2{}^S + \ldots \end{aligned}$$

by equation (12) above. Hence by equating these two values of $d\epsilon^S$ we obtain

$$\eta^S dt + sd\sigma + m_1{}^S d\mu_1 + m_2{}^S d\mu_2 + \ldots = 0,$$

which is equation [503] of Gibbs. Equation [508] is just another way of writing it. We have already seen that σ can be expressed as a function of the independent variables, t, μ_1, μ_2, etc., and [508] shows that if this function were known so that $\sigma = f(t, \mu_1, \mu_2, \ldots)$, where f is an ascertained functional form, then

$$\eta_S = -\frac{\partial f}{\partial t}, \quad \Gamma_1 = -\frac{\partial f}{\partial \mu_1}, \quad \Gamma_2 = -\frac{\partial f}{\partial \mu_2}, \quad \text{etc.} \tag{13}$$

Equation [508] is the "adsorption equation" and as we shall see presently the experimental verification of its validity is beset with difficulty and some doubt. One cause of this difficulty can be readily appreciated by considering the form of the equations (13) which constitute another way of expressing the Gibbs law of adsorption. Considering the first component, we see that its excess concentration in the surface (estimated of course per unit area) is given by the negative rate of change of the surface tension with respect to the potential of the first component in the adjacent phases, provided the temperature *and the remaining potentials* are not varied. Now, quite apart from the trouble involved in measuring with sufficient precision the excess concentration, it is impracticable to change the amounts of the components in the phases in such a manner that all but one of the potentials shall not vary.

15. Variations and Differentials

The apparent formal similarity of equations [497] and [501] should not blind the reader to the different implications of the two, which the alternative method of writing the derivation of [508] may help to bring out. In equation [497] the functional dependence in the mathematical sense of ϵ^S on the variables η^S, s, $m_1{}^S$, $m_2{}^S$, etc., is kept in the background as it were; $\delta\epsilon^S$, $\delta\eta^S$, $\delta m_1{}^S$, $\delta m_2{}^S$, etc., are any arbitrary *infinitesimal* variations of ϵ^S, etc., in other words, although ϵ^S is some function of the quantities η^S, s, $m_1{}^S$, $m_2{}^S$, etc., presumably discoverable by experiment, $\epsilon^S + \delta\epsilon^S$ is not necessarily equal to this same function of the quantities $\eta^S + \delta\eta^S$, $s + \delta s$, $m_1{}^S + \delta m_1{}^S$, $m_2{}^S + \delta m_2{}^S$, etc.; i.e., the varied state is not of necessity one of equilibrium. Equation [497], while being the statement of the condition that the unvaried state is one of equilibrium, is from the mathematical point of view a way of writing down the $n + 2$ partial differential equations (12). But in [501] the quantities $d\eta^S$, ds, $dm_1{}^S$, $dm_2{}^S$, etc. are not arbitrary variations but *differentials* whose values must be chosen so that the varied state is one of equilibrium as well as the initial, i.e., so that $\epsilon^S + d\epsilon^S$ is the same function of $\eta^S + d\eta^S$, $s + ds$, $m_1{}^S + dm_1{}^S$, $m_2{}^S + dm_2{}^S$, etc., as ϵ^S is of η^S, s, $m_1{}^S$, $m_2{}^S$, etc. If this is kept in mind it will be seen from the nature of the proof of [508] that, in passing from any state of the system for which [508] is assumed to be true to any other for which it is also true, we must pass through a series of equilibrium states; briefly all the changes involved must be reversible in the usual thermodynamic sense, not merely in the special sense in which Gibbs uses that word. More than one writer has pointed out that in some of the operations carried out in certain experiments made to test the validity of the adsorption equation this condition has apparently not been satisfied and irreversible steps have intervened. Further reference will be made to this presently, but it is this feature of the proof to which we have drawn attention that is involved.

16. Condition for Experimental Tests

In many of the experiments made to test the truth of [508] the adsorption is measured at the surface of bubbles of a gas or liquid rising through another liquid. Clearly such surfaces are not plane and yet in the argument it is generally implied that the conditions for a plane surface exist. Actually Gibbs has anticipated this point in his discussion on pages 231–233. The crucial point in this is reached on page 232 where he says "Now $\Gamma_1(c_1 + c_2)$ will generally be very small compared to $\gamma_1'' - \gamma_1'$." In general where adsorption is very marked Γ_1/ζ, which is the average *volume* concentration in the region of discontinuity, is greater than γ_1' or γ_1'', the volume concentrations in the homogeneous masses; but $\Gamma_1(c_1 + c_2)$ is of the same order of magnitude as Γ_1/R, where R is a radius of curvature of any curve in which a normal plane cuts the surface, and so $\Gamma_1(c_1 + c_2)$ has the same order of magnitude as Γ_1/ζ multiplied by ζ/R. If the thickness of the film is very small compared to R, the factor ζ/R may easily be less than the factor by which one would multiply γ_1' or γ_1'' to obtain Γ_1/ζ; so that $\Gamma_1(c_1 + c_2)$ is negligible compared to γ_1' or γ_1'' and therefore to their difference except in the rare cases where γ_1' and γ_1'' are extremely near to each other in value. Now even for small bubbles R must be much greater than ζ, and the conditions postulated would appear to be practically satisfied in the actual experiments. So that, although Gibbs says that "we cannot in general expect to determine the superficial density Γ_1 from its value $-(\partial\sigma/\partial\mu_1)_{t,\mu}$ by measurements of superficial tensions," the conditions which render this feasible in particular circumstances seem to be satisfied in the usual experiments, and we must look in other directions for the source of the discrepancies which undoubtedly exist. Of course, the first sentence of the next paragraph on page 233 which refers to the practical impossibility of measuring such small quantities as Γ_1, Γ_2, etc. has no application at present, as the skill of the experimenter has actually surmounted the difficulties.

17. *Importance of the Functional Form of σ in the Variables*

We have already pointed out that it is impracticable to obtain $\partial\sigma/\partial\mu_1$ directly by arranging to vary μ_1 while keeping the other potentials constant. Hence has arisen the device, actually suggested by Gibbs himself, of altering the position of the dividing surface from that which is termed the surface of tension to one determined so as to make a specified surface concentration vanish. This is fully expounded in pages 233–237. In the case of plane surfaces the term $C_1\delta c_1 + C_2\delta c_2$, which necessitated the special choice of the surface of tension, disappears in any case, and although ϵ_S, η_S, Γ_1, Γ_2, etc. will change in value with a change in the location of the dividing surface, σ will not change in value. To be sure, the proof given by Gibbs of this statement is confined to plane surfaces, but it is easily seen to be practically true even for surfaces of bubbles of not too great curvature; for on using the equation $p' - p'' = \sigma(c_1 + c_2)$ we see that the increment of σ caused by a change of amount λ in the position of the dividing surface, viz., $\lambda(\epsilon_V'' - \epsilon_V') - t\lambda(\eta_V'' - \eta_V') - \mu_1\lambda(\gamma_1'' - \gamma_1') -$ etc., is not actually zero, but equal to $\sigma\lambda(c_1 + c_2)$. As before, λ, which is in all cases comparable with the thickness of the discontinuous region, is so small that $\lambda(c_1 + c_2)$ is an insignificant fraction, and so σ is altered by a negligible fraction of itself. A difficulty, however, which might occur to an observant reader is the following. Since σ is a definite function of the variables t, μ_1, μ_2, etc., (for so it has been stated), how comes it that $\partial\sigma/\partial\mu_1$, $\partial\sigma/\partial\mu_2$, etc. will alter with the location of the dividing surface? We have just seen that σ does not alter, and certainly the variables t, μ_1, μ_2, etc. are in no way dependent on where we place the surface; if σ is a definite function of t, μ_1, μ_2, etc., so also are $\partial\sigma/\partial\mu_1$, $\partial\sigma/\partial\mu_2$, etc. definite functions of the same variables, and apparently they should no more change in value than σ itself. The solution of this difficulty requires the reader to guard against confusing the value of σ with the *functional form* of σ. Actually, if after the alteration σ remained a function of the variables t, μ_1, μ_2, etc., the implied criticism would be valid; but σ does not do so. It must be borne in mind, as indicated by Gibbs on page 235, that, with an alteration which makes Γ_1 zero, σ itself, although not changed in *value*, has to be regarded as an entirely different *function*, and moreover a function of the variables t, μ_2, μ_3, etc., μ_1 being excluded. The equation

$$p'(t, \mu_1, \mu_2, \ldots) = p''(t, \mu_1, \mu_2, \ldots)$$

enables us to express μ_1 in terms of t, μ_2, μ_3, etc. If this expression for μ_1 is substituted in the original function expressing σ, say $f(t, \mu_1, \mu_2, \ldots)$ we obtain an entirely different function say $\chi(t, \mu_2, \mu_3, \ldots)$. No doubt

$$f(t, \mu_1, \mu_2, \ldots) = \chi(t, \mu_2, \mu_3, \ldots),$$

but certainly $\partial f/\partial\mu_2$ is not equal to $\partial\chi/\partial\mu_2$, etc. The differential coefficients $\partial\chi/\partial\mu_2$, $\partial\chi/\partial\mu_3$, etc., are the new values of the surface concentrations (with reversed sign); there is of course no $\partial\chi/\partial\mu_1$ at all, in consequence of the fact that we have eliminated Γ_1; it has no existence. To be still more explicit the equation $p' = p''$ is by means of [93] equivalent to

$$\begin{aligned} &\epsilon_V' - t\eta_V' - \mu_1\gamma_1' - \mu_2\gamma_2' - \ldots \\ &\qquad = \epsilon_V'' - t\eta_V'' - \mu_1\gamma_1'' - \mu_2\gamma_2'' - \ldots \end{aligned} \tag{14}$$

Hence

$$\mu_1 = \frac{\epsilon_V' - \epsilon_V'' - t(\eta_V' - \eta_V'') - \mu_2(\gamma_2' - \gamma_2'') - \mu_3(\gamma_3' - \gamma_3'') - \ldots}{\gamma_1' - \gamma_1''}.$$

Inserting this value of μ_1 in $f(t, \mu_1, \mu_2, \ldots)$ we obtain $\chi(t, \mu_2, \mu_3, \ldots)$. We can then derive $\partial\chi/\partial\mu_2$ by observing that

$$\frac{\partial\chi}{\partial\mu_2} = \frac{\partial f}{\partial\mu_2} + \frac{\partial f}{\partial\mu_1}\frac{\partial\mu_1}{\partial\mu_2}$$

and obtaining $\partial\mu_1/\partial\mu_2$ in this result from (14). Thus

$$\frac{\partial\chi}{\partial\mu_2} = \frac{\partial f}{\partial\mu_2} - \frac{\partial f}{\partial\mu_1} \cdot \frac{\gamma_2' - \gamma_2''}{\gamma_1' - \gamma_1''},$$

so that

$$-\frac{\partial\chi}{\partial\mu_2} = \Gamma_2 - \Gamma_1\frac{\gamma_2' - \gamma_2''}{\gamma_1' - \gamma_1''},$$

which is equation [515], obtained by Gibbs in another way. We observe in passing that if the dividing surface is considered to be moved a distance λ toward the side to which the double accent refers we increase the amount of the rth component in the conceptual system, in which the two homogeneous phases are assumed to extend right up to the dividing surface, by $\lambda(\gamma_r' - \gamma_r'')$ estimated per unit area of the surface, and so we diminish the value of Γ_r by this amount, so that the new Γ_r is equal to the old $\Gamma_r - \lambda(\gamma_r' - \gamma_r'')$; if we choose λ to be equal to $\Gamma_1/(\gamma_1' - \gamma_1'')$, this obviously makes the new Γ_1 zero, and the new Γ_r, i.e. $\Gamma_{r(1)}$, equal to

$$\Gamma_r - \Gamma_1 \frac{\gamma_r' - \gamma_r''}{\gamma_1' - \gamma_1''},$$

which is the result [515] once more.

VII. Other Adsorption Equations

Having commented on the derivation and form of Gibbs' adsorption equation we will refer briefly to other equations, which have been suggested empirically or derived in other ways, concerning the concentration of components at a surface of discontinuity. Some of these refer to adsorption at solid surfaces just as much as at liquid surfaces; indeed in their derivation the conditions at solid surfaces have been more in the minds of their originators when developing their views. In such cases the concept of surface *tension* hardly has any bearing on the matter; but of course surface *energy* is a wholly justifiable term to use, although in the nature of things it is only at liquid-vapor or liquid-liquid interfaces that measurements of change of interfacial energy are practicable. This, however, is a minor matter, as it happens that the surface tension does not enter into many of these laws, apart from the one derived by J. J. Thomson, and a few others. Nevertheless, in the discussions concerning the validity of the Gibbs relation it is hardly possible to avoid making some reference to a few of these other proposed forms of adsorption laws, and that must serve as an excuse for making a brief reference to two or three of the most important of them. For a very adequate account of the complete group of laws the reader is referred to a review of the literature by Swan and Urquhart in the *Journal of Physical Chemistry,* **31**, 251–276 (1927).

18. The Exponential Adsorption Isotherm

Historically, the oldest equation is one usually referred to as the "exponential adsorption isotherm." We have already mentioned that Gibbs does not use the term "adsorption," and the word itself has been used somewhat loosely to cover effects complex in origin and due to the operation of more than one cause. It has been suggested that a rough criterion of adsorption proper is that it takes place very rapidly, whilst in many cases the effects produced by the presence of a porous substance such as charcoal immersed in a gas or gas-mixture or in a solution require considerable time to reach completion. McBain has suggested that the whole phenomenon should be called "sorption", and that portion of it which occurs rapidly should be termed adsorption proper. Rapidity of occurrence, however, can only be a rough guide at best. It is only in terms of the effect which Gibbs calls the "excess" (or defect in the case of negative adsorption or "desorption") of a component at a surface that a precise definition can be given. Actually adsorption is to some extent a phenomenon which recalls absorption, i.e., the dissolution of a gas or solute throughout the entire space occupied by a phase. Adsorption, however, differs from absorption in certain fundamental respects. As is well known, absorption equilibrium in a heterogeneous system is governed thermodynamically by a relation which demands (in the simplest case) that the ratio of the concentrations (or more exactly the activities) of a gas or solute in the different phases present shall be independent of the absolute quantity of gas or solute in the system. However, no such constancy obtains in a system consisting of an aqueous solution in which finely divided material such as charcoal is immersed; the concentration term of the solute in the aqueous phase has to be raised to a power less than unity in order to obtain a relation which is capable of fitting with sufficient accuracy the observed values of the adsorption. It is this relation which is called the "exponential" adsorption equation and is written in the form

$$x = kc^n ,$$

where x is the mass of gas or solute adsorbed per unit mass of adsorbing material, c the concentration of the solution in the bulk or the partial pressure of the gas in a gaseous system, n an exponent which in general is less than unity. The exponent n and the constant k are in general functions of temperature. For substances feebly adsorbable n approaches unity. Apparently this type of equation appears to have been first applied to adsorption of gases by Saussure as early as 1814, and in 1859 Boedecker extended it to solutions. It has since been employed by a large number of workers. The most complete examination of its applicability in relatively recent times has been made by Freundlich, whose name is now very generally associated with the relation itself. In his *Colloid and Capillary Chemistry* (English translation of the third German edition, p. 93 (1926)), he draws attention to the fact that some of the experimental results at liquid-liquid interfaces fit it fairly well; for in them there appears a striking feature, corresponding to what is known to be true at solid boundaries, viz., a surprisingly large relative amount adsorbed at low concentrations, followed by a growth as the concentration rises which is not in proportion to the concentration but increases much less rapidly, ending up at high concentrations with a saturation which hardly changes. Actually the exact formula is only roughly valid numerically at high concentrations, but when the conditions are sufficiently removed from saturation it holds quite well. Although only one of many relations suggested, it is still regarded as one of the most convenient and reasonably exact modes of representing existing data, especially for systems consisting of finely divided solids as adsorbing agents. For a discussion of the limitations of its applicability the reader is referred to Chapter V of *An Introduction to Surface Chemistry* by E. K. Rideal (1926).

19. Approximate Form of Gibbs' Equation and Thomson's Adsorption Equation

Actually Gibbs' equation is the earliest theoretically derived relation; but in 1888, about ten years after its publication, J. J. Thomson obtained by an entirely different method a relation which resembles that of Gibbs. There is a rather prevalent impression that the two equations are the same, but that is not so; and both on grounds of priority and because of the wider scope of Gibbs' result, there is no justification for the use of the name "Gibbs-Thomson equation" which one sometimes meets in the literature, although it is doubtless true that Thomson's work was independently carried out. In equations [217] and [218] Gibbs shows that, for a component the quantity of which is small, the value of the potential is given by an expression such as

$$A \log (Cm/v), \text{ or } A \log (m/v) + B\,,$$

where m/v is of course the volume concentration of the component in question and A, C (or B) are functions of the pressure, temperature, and the ratios of the quantities of the other components. For a dilute solution regarded as "ideal" this result becomes

$$\mu = \mu_0 + Rt \log c\,,$$

where c is the concentration of the solute and μ_0 is a function of pressure and temperature. This is proved in standard texts of physical chemistry. For non-ideal and concentrated solutions, the relation is given by

$$\mu = \mu_0 + Rt \log a\,,$$

where a is the "activity," whose value in any case can be determined by well-known methods described in the standard works. As the concentration diminishes the activity approaches the concentration in value. On this account an approximate form of Gibbs' equation is frequently used for a binary mixture, where the dividing surface is so placed that the surface concentration of one constituent (the solvent) is made zero. It is

$$\Gamma = -\frac{c}{Rt}\frac{d\sigma}{dc} \tag{15}$$

since $\delta\mu$ is put equal to $Rt\ \delta c/c$ if temperature and pressure do not vary. Now in Thomson's derivation of his result he uses the methods of general dynamics. The reader may be aware that in that science a system is specified by the coordinates and velocities or the coordinates and momenta of its discrete parts (the molecule, in the case of a physico-chemical system). The most usual method of attack on the problem of how its configuration will change in time is by the use of a group of differential equations which involve an important function of the coordinates and momenta which is called the Hamiltonian function. There is another method, however, actually developed by Lagrange before Hamilton's memoirs were written, which involves another group of differential equations associated with a function of the coordinates and velocities called the Lagrangian function. J. J. Thomson has made a brilliant application of this analysis to the discussion of the broad development of physico-chemical systems. Before the present-day methods of statistical mechanics had developed, he showed how to convert the actual Lagrangian function of a system into a "mean Lagrangian," expressed in terms of the physical properties of the system which are open to measurement, and by the aid of it to use the Lagrange equations so as to deduce macroscopic results. His work on this subject is summarized in his *Applications of Dynamics to Physics and Chemistry* (1888), a book that has never received the attention which it justly merited. By this method he deduced the following result for adsorption from a solution at its surface:

$$\frac{\rho'}{\rho} = \exp\left(\frac{s}{Rt}\frac{d\sigma}{d\xi}\right). \tag{16}$$

In deducing it he assumes that we have a thin film whose area is s and surface tension σ connected with the bulk of the liquid by a capillary tube. The quantity ξ is the mass of the solute in the thin film itself, while ρ and ρ' are the densities of the solute in the film and in the liquid, respectively. R is the gas constant for unit mass of the solute, i.e., the gram-molecular gas constant divided by the molecular weight of the solute. Now on studying Thomson's work we realize that his mean Lagrangian function is formulated for *dilute* solutions in which ideal laws are satisfied. This limitation enables us to transform (16) into the *approximate* form of Gibbs' relation. Provided ρ'/ρ is not very different from unity the argument of the exponential function is sufficiently small to permit us to write

$$1 + (s/Rt)\ (d\sigma/d\xi)$$

for the right-hand side of (16), and so

$$\frac{\rho - \rho'}{\rho} = -\frac{s}{Rt} \cdot \frac{d\sigma}{d\xi}.$$

Now, if the dividing surface is placed at the boundary between the film and the vapor, then $\rho - \rho'$ is the same as Γ/ζ, where ζ is the thickness of the surface film. Hence

$$\Gamma = -\rho \frac{s\zeta}{Rt} \frac{d\sigma}{d\xi}.$$

But $\xi/(s\zeta)$ is equal to ρ, and so

$$\Gamma = -\frac{\rho}{Rt} \frac{d\sigma}{d\rho}, \tag{17}$$

which under the limitations assumed is practically the approximate form of Gibbs' equation. The details of Thomson's work will be found in the *Applications*, Chapter XII. A critical inspection of the two formulae, Gibbs' and Thomson's, shows that they are not so similar as one imagines. We have already mentioned that the assumptions made concerning the dilute nature of the solution places a limitation on Thomson's result not ostensibly present in Gibbs'. Added to that, it is possible that the mathematical restrictions imposed by the neglect of higher powers in the expansion of the exponential function may place a further restriction on (17) which is more severe than that necessitated by the physical assumption concerning dilution. Thomson actually makes no quantitative application of his formulae—indeed in those days there were no data available; he draws from it just the same broad qualitative conclusions which can be inferred from Gibbs' result. If the presence of a solute lowers the value of the surface tension, so that $d\sigma/dc$ or $d\sigma/d\rho$ is negative, then Γ is positive by Gibbs' equation and $\rho' < \rho$ by (16), which we can write in the form

$$\left.\begin{aligned}\frac{\rho'}{\rho} &= \exp\left(\frac{1}{R\zeta t}\frac{d\sigma}{d\rho}\right)\\ &= \exp\left(\frac{1}{Rt}\frac{d\sigma}{d\kappa}\right)\end{aligned}\right\}, \tag{18}$$

where κ is the surface density of the solute, not in Gibbs' sense of an excess, but of the actual amount in the film. If, on the other hand, the surface tension is increased by increasing concentration of the solute, Γ is negative or $\rho' > \rho$, and the solution is less concentrated in the surface film than in the bulk of the phase; there is "desorption." Actually in the approximate form of Thomson's relation, viz. (17), σ is differentiated with respect to ρ, the equivalent of the volume concentration in the surface; to make it the exact counterpart of the approximate form of Gibbs' equation it should be

$$\Gamma = -\frac{\rho'}{Rt}\frac{d\sigma}{d\rho'}.$$

No doubt under the severe limitations imposed (which we have just referred to) this change is justified, but it is well to notice that in Thomson's actual result the concentration which is the variable on which σ depends is the surface concentration. In Gibbs' adsorption law the variable is the chemical potential and it matters not at all whether we refer to the potential at the surface or in the bulk of the phase, since by the equations of equilibrium they are equal; when we approximate we naturally use the approximation for the potential in terms of the bulk concentration. This indeed will serve as a cue to raise a small point which, as the writer knows from experience, occasionally causes some perplexity. The surface tension is of course measured *at the surface* and we cannot help feeling that it should be directly dependent on the concentration there. When one sees the expression $d\sigma/dc$ it is not altogether unpardonable to feel somehow that in this differential coefficient σ is the surface tension at the surface of a hypothetical solution in which there is no concentration at the surface. Any such idea must be carefully avoided. Such a condition would of course be physically unrealizable, and the conception is entirely valueless. To repeat it once more, σ is a function of t, μ_1, μ_2, etc., quantities whose values in the bulk of the solution are meant, and any approximations make σ still a function of physical variables as measured in the homogeneous mass. The writer is not aware that anyone has attempted to use Thomson's formula (16) or (18) in numerical calculation. The feature of it just mentioned would render it difficult; but if it were possible it would probably produce some improvement on the results calculated by the *approximate* form of Gibbs' relation. To show this suppose we write x for $(-1/Rt)\ (d\sigma/d\kappa)$; x will be positive when there is actually a surface excess, i.e., when $(d\sigma/d\kappa)$ is negative. Equation (18) would then be

$$\frac{\rho}{\rho'} = e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$$

The approximation would be

$$\frac{\rho}{\rho'} = 1 + x.$$

Clearly, since x is positive, the values of ρ obtained from the first of these would be markedly larger than those obtained from the second if x were not entirely negligible compared to unity, and it is well-known that even in those experimental results which show the best accord between observation and calculation the tendency is for the observed concentration to be above that calculated by the approximate form of Gibbs' equation, which the second of the above equations most resembles.

It also merits attention that Thomson's equation can be readily obtained by the present-day methods of statistical mechanics in a very direct way. If the reader will look once more at section IV of this article (Article L) under the heading "Statistical Considerations" he will observe in equation (10) how the concentrations in two phases are related in simple cases to the work required to extract a molecule from one phase and introduce it into another. Now in the present instance the solution in bulk may be regarded as the second phase and the surface film the first; σ is the surface energy per unit area of the film, meaning by that the energy possessed by the molecules in unit area of the film in excess of what they would possess if they were in the body of the fluid. Hence the $d\sigma$ in (18) will refer to an increase in this, i.e., the work required to extract from the bulk and bring to the surface a number of molecules given by $N\zeta d\rho$, where N is the number of molecules in unit mass of the solute; for ζ is equal to the volume of unit area of the film and $\zeta d\rho$ the increase in the mass of the solute in it. Hence, since R refers to the gas constant for unit mass of the solute,

$$R\zeta d\rho = Nk\zeta d\rho,$$

and we see that $(1/R)\ (d\sigma/d\kappa)$ is equal to the work required to bring one molecule from the interior to the surface divided by k, i.e., to $\{\theta(n_1) - \theta(n_2)\}/k$. Thus by (10)

$$\frac{\rho}{\rho'} = \exp\left(-\frac{1}{Rt}\frac{d\sigma}{d\kappa}\right),$$

which is just Thomson's equation. Thus, not only in the form of the equation but also in the possibility of deducing it in this way, one might state with some show of reason that it is really more akin to some recent results obtained by Langmuir and others than to Gibbs' law.

It should be mentioned as a matter of interest that Warburg in 1890 made use of an equation, which is virtually Gibbs' approximate result, in his well-known paper on "Galvanic Polarization" (*Ann. d. Physik*, **41**, 1, (1890)). By means of it he made some calculations on the forcing of the solute out of the surface layer in the case of inorganic salts which raise the surface tension of water and so are desorbed. He used a thermodynamical argument; in an addendum to the paper he refers to the earlier proofs of Gibbs and Thomson.

Quite a number of proofs of Gibbs' equation, usually in the approximate form, have been published from time to time. (See Swan and Urquhart's paper cited above.) Porter, in the *Trans. Faraday Soc.*, **11**, 51, (1915), has derived an equation for concentrated solutions, viz.,

$$\Gamma = -\frac{(1 - ac)^2}{Rt}\frac{d\sigma}{dc},$$

where c is the ratio of solute molecules to solvent molecules and a is a factor obtained from the equation

$$\frac{c}{1 - ac} = \log\frac{P}{p},$$

P being the saturation pressure of an adsorbed gas or vapor and p its equilibrium pressure. In this the departure from the simple approximate Gibbs' formula is attributed to the formation of loose compounds between the molecules of the solute and those of the solvent, which is termed solvation. This has the effect of altering the internal pressure of the solution and with it other properties such as surface tension and compressibility which depend upon the internal pressure. On account of the existence of this solvation Freundlich has criticized the approximate form of Gibbs' law even for dilute solutions, since this property certainly interferes with the application of the simple van't Hoff laws to them. Langmuir, however, has replied to this criticism by pointing out that there are derivations of the law, e.g. Milner's, in which the gas laws are applied only to the interior of the solution. This, of course, does not invalidate in any case the complete form of Gibbs' law, although even this is almost certainly limited to true solutions and cannot be applied to colloidal solutions. This point has been emphasized by Bancroft (*J. Franklin Inst.*, **185**, 218, (1918)); we have already drawn attention to the feature of the proof which implies thermodynamic reversibility of the adsorption process, and that is certainly in doubt in some instances where the equation has been applied. Undoubtedly in true solutions some equation of the form

$$\Gamma = -f(c, t)\frac{d\sigma}{dc}$$

holds, where $f(c, t)$ is some function which is positive; but this cannot be formulated correctly until a general formula for potential in terms of concentration has been discovered.

20. The Empirical Laws of Milner and of Szyszkowski for σ and c. Langmuir's Adsorption Equation. Frenkel's Equation

We shall now turn for a moment to one or two empirical relations between surface tension and bulk concentration in solutions. For relatively strong solutions of acetic acid Milner (*Phil. Mag.*, **13**, 96 (1907)) found that a formula of the type

$$\sigma_0 - \sigma = \alpha + \beta \log c$$

was satisfied, where σ_0 is the surface tension of water, σ that of a solution of concentration c, and α and β are constants. Shortly after, Szyszkowski (*Z. physik. Chem.*, **64**, 385, (1908)) suggested a somewhat different form, viz.,

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log\left(1 + \frac{c}{a}\right),$$

where a and b are constants. He verified this for solutions of the shorter-chain normal fatty acids. It was observed that the constant b had the same value for all the acids, while a was different for each acid. Its values, however, for two acids differing by one carbon atom bore a nearly constant ratio, the three carbon acid having an a 3.4 times larger than the a for the four carbon acid, and so on. This means that $1 + (c/a)$ is a larger quantity for the same concentration the longer the hydrocarbon chain in the acid, and so in this homologous series of acids the diminution of surface tension at a given concentration increases rapidly in amount as the hydrocarbon chains are lengthened, which is just an example of a well-known rule due to Traube that the capillary activity of a member of an homologous series increases strongly and regularly as we ascend the series. For by the Gibbs' simple formula

$$\begin{aligned}\Gamma &= -\frac{c}{Rt}\frac{d\sigma}{dc}\\ &= \frac{b\sigma_0}{Rt}\cdot\frac{c}{c+a}.\end{aligned}$$

Thus to obtain the same surface concentration we require for each successively higher member of the series a bulk concentration about one third of that of the previous member, and so the higher members are more and more "capillary active," to use a common term which designates the property of causing a lowering of surface tension and being in consequence adsorbed in excess quantity at the surface. It will be observed that, if c is large compared to a, Szyszkowski's formula approximates to that of Milner. A relation has just been found from the former, viz.,

$$\Gamma = g \frac{c}{c + a}, \tag{19}$$

where g is a constant at given temperature and would be in fact the upper limiting value of Γ if the law held for extremely high concentrations. Now this relation is virtually equivalent to an equation deduced by Langmuir (*J. Am. Chem. Soc.*, **38**, 2221, (1916)) for the adsorption of gases on a *solid* surface (plane crystalline). Although not of special interest now, it may not be amiss to indicate Langmuir's argument in broad fashion, inasmuch as Gibbs at a later point in his treatment deals with the conditions at a surface separating a solid from a fluid.

Langmuir's special hypothesis is that the molecules of the gas are "condensed" on the crystalline surface when they strike it, and do not in fact rebound in an elastic fashion as sometimes postulated in kinetic theory of gases, except in a minority of impacts. There is a good deal of evidence that this is actually the case, and that in general the molecules remain on the surface for a longer or shorter time depending on the attractive forces between the solid and the adsorbed layer, and on the temperature. There is therefore a concentration of molecules on the surface whose amount depends on the average length of time during which the molecules remain upon it. This state of affairs obviously resembles what happens when molecules of a solute pass from the solution into the surface layer and so it is not surprising that there should be a formal resemblance in the laws deduced in the two cases. Indeed Langmuir's analysis could be easily adapted to give a theoretical foundation for

Szyszkowski's formula in the latter case. A further assumption is that the adsorbed layer is one molecule thick and that no further adsorption occurs in a second layer beyond this. This assumption is also in keeping with what are nowadays believed to be the conditions at the surface of a solution, a matter to which we shall devote some attention later on, as it is one on which Gibbs' equation brings important considerations to bear. Let a fraction θ of the surface be covered with adsorbed gas, and the rate at which molecules evaporate from unit area of the adsorbed layer be $\alpha\theta$, α being a function of the temperature and depending also on the attractive forces. The rate at which gas molecules impinge on unit area of the surface is proportional to the density of the gas and the average molecular velocity, i.e., to $\rho t^{\frac{1}{2}}$ (t is the absolute temperature). Since $p = \rho t$ this rate is therefore proportional to $p/t^{\frac{1}{2}}$. Therefore the rate of condensation (which by the postulates we take to be comparable with and proportional to the rate of impact) on unit area of the *bare* surface can be written as $\beta p t^{-\frac{1}{2}}$, where β is a constant. We suppose that no condensation occurs on the top of an adsorbed layer. (That is the second postulate above and assumes that the attractive forces of the solid do not extend appreciably through the first layer,—a reasonable assumption on our present knowledge.) Thus the rate of condensation on unit area of the surface of the adsorbed layer will be

$$\beta p t^{-\frac{1}{2}}(1 - \theta)$$

since a fraction $1 - \theta$ is bare. Hence in equilibrium

$$\beta p t^{-\frac{1}{2}}(1 - \theta) = \alpha\theta\,,$$

from which we easily obtain

$$\theta = \frac{p}{p + \dfrac{\alpha}{\beta} t^{\frac{1}{2}}}$$

$$= \frac{p}{p + a}\,,$$

where a is a constant depending on attractive forces and temperature. If n is the number of molecules actually adsorbed per unit area at any moment, and n_m the maximum number which could possibly be adsorbed if the unit area were entirely covered with a monomolecular layer, θ is n/n_m, and so Langmuir's result can be written

$$n = n_m \frac{p}{p + a}. \tag{20}$$

The result is of considerable theoretical importance in connection with the so-called "poisoning" of solid catalysts. The formal similarity of (19) and (20) is obvious, the pressure of the gas being the analogue of solution concentration in (19). As stated above, Langmuir's analysis could easily be adapted to prove (19) and so by the aid of Gibbs' equation to derive Szyszkowski's relation. Frenkel in the *Zeit. f. Physik,* **26, 117,** (1924) derives a special functional form for the constant a in (20). On certain assumptions he shows that the mean length of time during which a molecule adheres to the surface is equal to $\tau \exp (u/kt)$, where τ is the period of thermal oscillation, at right angles to the surface, of an adsorbed molecule, u the energy of desorption, i.e., the energy required to tear an adsorbed molecule away, and k the gas constant per molecule. Thus the rate of evaporation from unit area is $n/[\tau \exp (u/kt)]$ and so the constant α is equal to $\tau^{-1} \exp (-u/kt)$. Also it can be shown from the kinetic theory of gases that $\beta = (2\pi mk)^{-\frac{1}{2}}$, where m is the mass of a molecule. Hence Frenkel's form of Langmuir's result can be written

$$n = n_m \frac{p}{p + \dfrac{(2\pi mk)^{\frac{1}{2}}}{\tau} e^{-\frac{u}{kt}}}.$$

For further information on these and similar equations the reader can consult Chapter V of Rideal's *Surface Chemistry* and Chapter VIII of Adam's *Physics and Chemistry of Surfaces* (1930).

21. Energy of Adsorption

Returning to adsorption at the surfaces of solutions, it has already been stated that Thomson's equation has a close kinship with some equations of Langmuir and others. We can enlarge a little on this point. The surface film of a liquid is a region where the potential energy of a molecule of the solute is greater by a definite amount ϵ than that possessed by the molecule when in the bulk of the solution. It follows from the fundamental statistical law that since Γ/ζ is the volume concentration in the film

$$\frac{\Gamma}{\zeta} = c \exp\left(-\frac{\epsilon}{kt}\right)$$

or

$$\epsilon = -kt \log \frac{\Gamma}{\zeta c} \cdot$$

Langmuir has applied this result to Szyszkowski's measurements of the surface tensions of solutions of the fatty acids and to the adsorptions calculated therefrom. If ϵ_n and ϵ_{n-1} are the energies of adsorption per molecule for acids with n and $n - 1$ carbon atoms, respectively, then

$$\epsilon_n - \epsilon_{n-1} = -kt\left\{\log\left(\frac{\Gamma}{c}\right)_n - \log\left(\frac{\Gamma}{c}\right)_{n-1}\right\},$$

assuming that the film thickness ζ is the same in all cases. In the case of dilute solutions where c is small compared to a this result becomes by (19)

$$\epsilon_n - \epsilon_{n-1} = -kt\{\log a_{n-1} - \log a_n\},$$

since g, i.e. $b\sigma_0/Rt$, is the same for all the acids. Now, as mentioned above, a_{n-1}/a_n has an almost constant value about 3.4, so that $\log a_{n-1} - \log a_n$ is the same for any pair of successive acids. Thus the energy of adsorption increases by a constant amount for each CH_2 group added to the hydrocarbon chain of fatty acids. "This must mean that each CH_2 group is situated in the same relation to the surface as every other such group in the chain, and this can only be the case if chains lie parallel to the surface. Hence Langmuir concluded that the molecules lie flat in the surface, in the gaseous adsorbed films."*

Equation (19) is an example of an adsorption law deducible from statistical considerations. We shall bring these references to such equations to a conclusion by adapting an argument to be found in Rideal's *Surface Chemistry*, p. 71, which leads to another example of them. Let there be n_1 molecules of a solute in the surface layer of thickness ζ and area s, and n_2 molecules of solute in a volume V of the solution. If the layer is of the unimolecular type, the evidence for which we shall discuss in the next section, there is a free volume in it of amount $s\zeta - n_1v$, where v is the effective volume of one molecule. If we add some more molecules to the solution there will be a division into two groups; one whose number is δn_1 will be found in the layer, one whose number is δn_2 will be found in the solution. The volume concentration of the first group will be $\delta n_1/(s\zeta - n_1v)$, of the second $\delta n_2/V$, and these two concentrations will have the ratio $\exp(-u/kt)$ where u is the energy of adsorption; i.e.,

$$\frac{\delta n_1}{s\zeta - n_1v} = \frac{\delta n_2}{V}\lambda,$$

λ being written for $\exp(-u/kt)$. By integration we obtain

$$\begin{aligned}\log(s\zeta - n_1v) &= -\frac{\lambda n_2 v}{V} + \text{constant}\\ &= -\lambda vc + \text{constant},\end{aligned}$$

where c is the bulk concentration. Hence

$$s\zeta - n_1v = Ce^{-\lambda vc}.$$

Since n_1 is zero when c vanishes, $C = s\zeta$ and therefore

$$n_1v = s\zeta(1 - e^{-\lambda vc})$$

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* Quoted from page 128 of Adam's *Physics and Chemistry of Surfaces*. The reader must not interpret "gaseous adsorbed" as meaning adsorbed from the superincumbent gas. It is a term applied to a special type of film, of which we shall say more at a later stage.

or

$$\left.\begin{aligned}\frac{n_1}{s} &= \frac{\zeta}{v}\,(1 - e^{-\lambda vc}) \\ &= g\,(1 - e^{-ac}),\end{aligned}\right\} \tag{21}$$

where g and a are constants.

We see that this adsorption isotherm has the same feature as (19), viz., that n_1/s the surface concentration of the solute approaches a limiting value g as c increases. In fact, since g is ζ/v, we see by the definitions of ζ and v that g is the surface concentration when the assumed unimolecular layer is quite full. By measurements of the surface and bulk concentrations at different states of dilution where the equation is valid we can eliminate g and measure the constant a. By repeating these measurements at another temperature we can determine the value of a at this other temperature, say a' at temperature t'. This gives us the ratio λ'/λ which is of course equal to a'/a. But $\lambda = \exp(-u/kt)$; hence we obtain

$$\frac{u}{kt} - \frac{u}{kt'} = \log\,(\lambda'/\lambda)$$

and knowing k, t and t' we can obtain u the energy of adsorption.

VIII. Experimental Investigations to Test the Validity of Gibbs' Adsorption Equation

22. The Earlier Experiments to Test Gibbs' Equation

The simplest conditions from a theoretical point of view for testing the Gibbs equation exist at the boundary separating a vapor from a liquid; however, this is not the easiest case to test by experiment, and measurements carried out at air-liquid or liquid-liquid interfaces make up the majority of the attempts in this direction. When we have a binary mixture, the equation becomes (at constant temperature)

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2.$$

As we have seen, this is only strictly valid for the surface of tension determined in the manner pointed out earlier. Practically, however, any surface in the film will serve, provided that the values of Γ_1 and Γ_2 are adapted, as we have shown, to the chosen situation. It has been customary to choose the position of the surface so that the actual amount of one of the components in the discontinuous region is the same as if its density were uniform in each phase right up to the surface. This makes one of the excess concentrations (say Γ_1) zero, and the equation becomes

$$d\sigma = -\Gamma_{2(1)}\, d\mu_2 .$$

Gibbs, himself, originally suggested this procedure and gives an example of its application in the footnote to page 235. In a number of the measurements, the simple formula for the chemical potential

$$\mu = \mu_0 + Rt \log c$$

has been used, and these on the whole indicate that a solute which lowers surface or interfacial tension is concentrated more at the surface than is deduced by the use of this formula. Measurements of the activity of solutes are not yet very numerous, but wherever the more accurate expression for the potential

$$\mu = \mu_0 + Rt \log a$$

can be used, the agreement is very much better, though there still appears to be a greater concentration than the equation would lead us to expect. However, in addition to direct tests of the validity of the equation, it has been used to investigate the structure of the surface region, and the comparison of the results with the properties of films of insoluble substances at the surface of a liquid, obtained by Langmuir, Adam and others by different means, seems to lend considerable support to its validity.

There are a number of early investigations which show that a concentration of capillary-active solutes at the surface actually does take place. Plateau (*Pogg. Ann.*, **141**, 44, (1870)) showed that the viscosity of the surface layers of a saponin solution in water was greater than in the interior. Zawidski (*Zeit. physik. Chem.*, **35**, 77, (1900) and **42**, 612, (1903)) prepared saponin foams and showed by means of measurements of the refractive index that the saponin content in the foam was higher than in the original solution. Analogous qualitative information was obtained by Ramsden (*Zeit. physik. Chem.*, **47**, 336, (1904)) on the accumulation and consequent precipitation of protein at surfaces. C. Benson (*J. Phys. Chem.*, **7**, 532, (1903)) examined foams from aqueous solutions of amyl alcohol and also observed excess concentration of the alcohol in the foam. An important investigation was made by S. R. Milner (*Phil. Mag.*, **13**, 96, (1907)) on solutions of acetic acid and sodium oleate. He used the Gibbs equation in its simple form to calculate the surface excess in the first case and brought out the important fact that the surface excess for a normal solution of acetic acid is only about 15 per cent less than what it is for a solution eight times as concentrated. In the case of sodium oleate, its high capillary activity causes the surface tension to fall so rapidly that the (σ, c) curve quickly becomes nearly parallel to the c-axis, and only very doubtful values of Γ could be obtained. A rough experimental method gave as the surface excess 0.4 mgm. per square meter, which Milner regarded as a "moderately good estimate" for it at the moment of formation of the bubbles of air which were passed through the oleate solution; but he was of the opinion that this was "very much less than the ultimate value of the excess." He concluded that there was an irreversible process here which actually caused the solute to come out of solution in the surface in consequence of excessive adsorption. As we have pointed out above, if such is the case the theoretical conditions for an application of Gibbs' equation do not hold under these circumstances.

Actually the first attempts at a *quantitative* verification of the equation were made by W. C. M. Lewis at the suggestion of Donnan (*Phil. Mag.*, **15**, 499, (1908) and **17**, 466, (1909)). In one set of experiments an oil-water interface was used and solutes were chosen so as to be insoluble in the oil phase and very capillary-active in the aqueous phase. Sodium glycocholate, however, yielded results for the direct measurement of

Γ which were about 80 times as great as those calculated on the basis of Gibbs' equation. The sodium salt of congo red, methyl orange and sodium oleate were also tried and exhibited a similar though less marked discrepancy. Despite the experimental difficulties of the tests, there was no possibility of ascribing these results to experimental errors or to the use of the simple form of the equation. The excessive adsorption was almost certainly a characteristic of the semi-colloidal solutes employed. Subsequently Lewis used a solute of much simpler constitution, and one truly soluble in the aqueous medium, viz. aniline, and measured the adsorption at a mercury-water interface (*Zeit. physik. Chem.*, **73**, 129, (1910)). The calculated and observed adsorption values now showed agreement as regards order of magnitude, both being small multiples of 10^{-8} grams per sq. cm.

A still more successful test was carried out by Donnan and J. T. Barker (*Proc. Roy. Soc.*, **85 A**, 557, (1911)) who measured the adsorption of nonylic acid at an air-water surface. The Γ was evaluated from the expression $(-c/Rt)\ (d\sigma/dc)$ and calculated, first, on the assumption of non-ionization of the acid and, second, on the assumption of complete ionization. The table gives the observed and calculated values.

ADSORPTION OF NONYLIC ACID AT AIR-WATER SURFACE

Percentage Concentration in Solution	$\Gamma \times 10^7$ obs.	$\Gamma \times 10^7$ calc.	
		(1)	(2)
0.00243	0.95	0.55	0.26
0.00500	1.52	1.14	0.57
0.00759	1.09	1.26	0.63
0.00806	0.915	—	—

Donnan and Barker also measured the adsorption of the glucoside saponin at an air-water surface; this forms very stable foams and viscous films at the bounding surface of air bubbles. There was agreement between the orders of magnitude of Γ observed and calculated, but from a substance of this character little more could be expected, and the results with nonylic acid are of greater value.

Patrick (*Zeit. physik. Chem.*, **86**, 545, (1914)) investigated the behavior of mercurous sulphate, salicylic acid and picric acid at a mercury-water interface, but the experiments only gave qualitative results from our point of view, as a quantitative estimate of Γ could not be made. Later, Patrick and Bachman (*Journ. Phys. Chem.*, **30**, 134, (1926)) found that the cation is more readily adsorbed than the anion of a mercurous salt at a mercury-water interface.

Frumkin in *Zeit. physik. Chem.*, **116**, 498, (1925) described a method for testing the law which differed considerably in the experimental procedure from those previously used. He worked with lauric acid, chosen because of its relatively slight solubility in water, and managed to produce a saturated layer of the acid on the water whose concentration he could measure, obtaining an adsorption of 5.2×10^{-10} moles per sq. cm. Using the (σ, c) curve in the neighborhood of saturation he calculated Γ to be 5.7×10^{-10} moles per sq. cm. He made control experiments to test the accuracy of his measurements and concluded that the error in the calculated value was not more than 10 per cent, and that about the same uncertainty affected the observed amount. If this is so, Frumkin's measurements constitute one of the most satisfactory tests yet made.

Reference should also be made to some experiments made by Bancelin (*J. chim. phys.*, **22**, 518, (1925)) on the adsorption of dyestuffs (at very low bulk concentration) both at liquid-air and liquid-mercury interfaces. Rather remarkably, Bancelin obtained fair agreement between calculated and observed values for these solutes.

Historically, the next important contribution is that of Schofield (*Phil. Mag.*, **1**, 641, (1926)), who observed the adsorption by mercury of its own ions from solution. However, in this work we are concerned with somewhat wider issues than those raised by the Gibbs *capillary* adsorption equation. Questions concerning the electric potentials at the surface enter into the discussion, and we shall postpone dealing with these until we treat electrocapillarity towards the end of this article.

23. The Experiments of McBain and His Collaborators

The most extensive and exact experimental test of Gibbs' equation carried out up to the present is that of McBain and Davies (*J. Am. Chem. Soc.*, **49**, 2230, (1927)). Brief accounts of it will be found in the books by Adam and Rideal. The substances examined were aqueous solutions of *p*-toluidine, of amyl alcohol and of camphor. The method used for determining Γ was the bubble method much improved as to accuracy over previous investigations, an accuracy of a few per cent being claimed. If this is so, there is no doubt that these experiments have left the whole matter in some doubt. Hitherto, it had been regarded as very satisfactory that an agreement in order of magnitude between calculated and observed values had been reached, in view of the manifest difficulty of the measurement of the adsorbed amounts. If the claim to high accuracy made by McBain and his co-workers is justified, this state of satisfaction is hardly possible any longer. The general idea of the method is that bubbles of very pure nitrogen saturated with the vapors of the solution are passed up a long inclined tube of large diameter containing the solution. The slope of the tube is adjusted so that the time occupied by the bubbles in passing to the top end of the tube is amply sufficient to insure that the surface of each bubble has attained the full adsorption concentration corresponding to the bulk concentration of the solution, the tube being so large that the adsorption does not appreciably lower this bulk concentration. At the top of the incline the bubbles rise into a vertical tube so narrow that each bubble fills its diameter. Each bubble in the vertical tube rapidly overtakes its predecessors and draining is so rapid that within a few inches there is a continuous column of cylindrical bubbles in contact with one another. At the height at which draining is found to be sufficiently complete the narrow tube is curved over and down. The films break in the downward portion of the tube and collapse to a liquid which is caught and analyzed. For a full account of the very stringent precautions taken to insure accuracy the literature should be consulted. It must be admitted that little was left undone in that direction. Perhaps the only possible source of trouble has been indicated by Harkins (*Colloid Symposium Monograph,* **6**, 36, (1928)). As bubbles pass along the tube, they oscillate in shape; this involves an oscillation in the extent of the drop surface. Suppose that saturation in adsorption were attained when the surface is at its maximum value, then when a subsequent contraction takes place the compression (in two dimensions) thereby produced might cause some of the adsorbed material to gather into droplets on the surface, and so more of it would accumulate on the surface than would correspond to true adsorption. Be that as it may, the general nature of McBain's results may be indicated broadly thus:

Firstly, the calculated value of Γ tends to a maximum as the bulk concentration increases. Actually this might be anticipated from the equation of Szyszkowski quoted earlier. Thus according to it

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log \left(1 + \frac{c}{a}\right),$$

and

$$\Gamma = \frac{b\sigma_0}{Rt} \frac{c}{c + a},$$

which approaches a limit $b\sigma_0/Rt$ as c increases.

Secondly, the observed values of Γ also rise to a maximum, but during the whole course of events are definitely greater than Γ calculated. The table for *p*-toluidine shows this.

Concentration of Solution (in grams per liter)	$\Gamma \times 10^8$ obs. (in grams per sq. cm.)	$\Gamma \times 10^8$ calc.
0.6	2.4	1.5
1.0	6.5	4.7
1.4	10.4	6.6
2.0	12.7	6.8
3.0	13.4	7.1
4.0	13.2	7.3
5.0	13.0	7.5
6.0 (saturated)		

The results for camphor show also a discrepancy of about two to one; while for amyl alcohol the discrepancy is still greater, amounting to about four or five to one.

At first McBain regarded this discrepancy as due, in part at all events, to the approximate character of the expression $(-c/Rt)(d\sigma/dc)$ which was used for Γ calculated; but in a later paper with Wynne-Jones and Pollard (*Coll. Symp. Monograph*, **6**, 57, (1928)) he abandons this explanation, as it was found for *p*-toluidine that its partial vapor pressure over an aqueous solution was directly proportional to the concentration of the solute. This partial pressure gives a direct measure of the activity of the dissolved *p*-toluidine and so there is no difference in value between $c(d\sigma/dc)$ and $a(d\sigma/da)$. That being so, McBain repeated still more decidedly a suggestion which he had already made tentatively in the first paper, viz., that the situation is complicated by the existence of surface electrification effects, and that the omission of any consideration of these vitiates the theoretical basis of the adsorption equation, as it stands, without an additional differential term on the right-hand side representing increase in the energy of this surface electrification when concentration increases by a differential amount. We cannot deal with this point now, but will return to it at a later stage of this commentary. A further point raised by McBain and Davies (*loc. cit.*) is that in these and similar experiments "seldom or never have true, two-component systems been actually under observation, although this is fundamental. Solutions of electrolytes or substances capable of hydrolysis, such as soap, cannot be treated as two component systems except in the rare event that the composition of the adsorbed material is identical with that of the solute remaining in the solution." The point of this remark is that we are implicitly using the equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

and making Γ_1 zero by adjusting the surface so that we have

$$d\sigma = -\Gamma_{2(1)}\, d\mu_2.$$

But this is invalid if there are still other components present. As McBain and Davies say "The component (or components) actually present, but hitherto ignored, is the gas (or air) in presence of which the surface tension is measured when bubbles are produced." If we set Γ_1 for the solvent equal to zero there are at least two other components (such as *p*-toluidine and nitrogen); "their adsorption is $\Gamma_2 = -(\partial\sigma/\partial\mu_2)_{\mu_3}$ and $\Gamma_3 = -(\partial\sigma/\partial\mu_3)_{\mu_2}$ each of which is readily measured, although this has never been done. It is obvious that the two adsorptions will mutually interfere. . . . For example, it has been stated that the surface tension of mercury is 10 per cent lower in the presence of one atmosphere of nitrogen than *in vacuo*; similarly, nitrogen lowers the surface tension of water by about one per cent, which would correspond to the adsorption of about 3 per cent as many molecules of nitrogen as of *p*-toluidine. However, such mutual interference cannot explain the high values of the observed adsorptions."

As it can be stated here that McBain's explanation of the discrepancies in terms of surface electrification effects has not been universally accepted, it is clear that the evidence for the complete quantitative validity of Gibbs' law, as against a rough qualitative agreement, is far from satisfactory. In reflecting on the various theoretical steps in the proof one naturally feels somewhat dubious about the arbitrary placing of the surface of division in order to get rid of one term in the differential expression; in discussing these matters the writer has, for example, heard such statements as these: "Nature fixes the surface; surely we cannot mess it about as we please." There is something to be said for this instinctive recoil from a procedure apparently so arbitrary; yet a close investigation leaves us little hope of evading our difficulties by pressing this instinct into our service. For instance, let us look at Gibbs' equation [515], where the strictly placed dividing surface is used, showing us that

$$\Gamma_{2(1)} = \Gamma_2 - \Gamma_1 \frac{\gamma_2' - \gamma_2''}{\gamma_1' - \gamma_1''}.$$

In this $\Gamma_{2(1)}$ is the surface excess as calculated, while Γ_2 is what we might call, if we were disposed to press the point we are presenting, the "true" surface excess, and it would appear that Γ_2 is greater than $\Gamma_{2(1)}$ provided Γ_1 is positive, which is certainly in the right direction for an elucidation of the mystery. The value of γ_1'', the concentration of the solvent in the vapor phase in the gas-liquid experiments, is negligible compared to γ_1', so that Γ_2 exceeds $\Gamma_{2(1)}$ by $(\gamma_2' - \gamma_2'')\Gamma_1/\gamma_1'$. Until we know something about Γ_1 we cannot say whether this is going to improve matters or not. We shall have occasion in the following section to return to this point, which we leave for the present.

IX. Gibbs' Equation and the Structure of Adsorbed Films

24. Impermeable or Insoluble Films

On pages 275, 276 Gibbs makes a very brief allusion to "impermeable films" which may offer an obstacle to the passage of some of the components from one phase to the other. "Such may be the case, for example, when a film of oil is spread on a surface of water, even when the film is too thin to exhibit the properties of the oil in mass." The latter part of this sentence is most significant in view of subsequent events. Gibbs contents himself with pointing out that for any component which is found on both sides of the film, but which cannot pass the film itself, the potentials on either side cannot be proved to be equal, and so in the adsorption equation, for example, a single term such as $-\Gamma_1 d\mu_1$ must be replaced by $-\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$, where Γ_1 and Γ_2 refer to the surface excesses of the *same component* on the two sides of the dividing surface and μ_1 and μ_2 indicate the differing potentials in each adjacent phase.

Soon after the existence of "surface tension" became known, it was discovered that oil films on water reduced this property very markedly. This is of course quite a different phenomenon from the lowering by capillary-active soluble substances. It was Rayleigh who began accurate experimental work on the thickness of such oil films (*Proc. Roy. Soc.*, **47**, 364, (1890)). Some very important results were discovered by Miss Pockels who was the first to use the method of "barriers," which by resting just on the surface of a liquid in a trough and extending over its whole width could be used to push a surface film in front of them so that it could be compressed or extended in two dimensions (*Nature*, **43**, 437, (1891)). She made the discovery that provided the area of a film formed by a small given quantity of oil exceeded a certain critical value the surface tension did not differ appreciably from that of water, but as the area was reduced below this value, the surface tension fell rapidly. Later, Rayleigh (*Phil. Mag.*, **48**, 321, (1899)) suggested that at this critical area the molecules are just crowded into a layer one molecule thick; that they are in fact floating objects which begin to repel one another when coming into contact in a single layer. This accounts for the first appearance of a diminution in surface tension at this point; a barrier moving a small distance in the direction of the pressure arising from this would gain kinetic energy, presently dissipated in the general body of the fluid. The corresponding loss of energy will be found in the fact that the expanding surface covered by oil will not gain as much surface energy as is lost at the contracting clean surface, which is merely a statement of the fact that the oil covered surface has a smaller "surface tension" than the clean, but does not imply the existence of a physical tangential pull in the surface. Actually, as Devaux was the first to point out, some films may acquire the properties of a two-dimensional solid possessing a tangential rigidity in the surface which prevents them being blown about into differing shapes.

25. The Work of Langmuir and Adam. The Concept of "Surface Pressure." Equations of Condition for Surface Phases

Great improvements in the experimental appliances were introduced by Langmuir (*J. Am. Chem. Soc.*, **39**, 1848, (1917)) so that it became possible to measure these small surface pressures, and his work has been extended with great success by Adam. In Adam's book, already cited, will be found an account of his work with references to the numerous papers by himself and his co-workers. In the most recent form of Adam's apparatus surface pressures as small as 0.01 dyne per cm. can be measured. Also a great many tests have been made with substances which are simpler than oils and whose chemical constitution is better known. It is possible actually to give the results in terms of the surface pressure corresponding to the area of surface covered by a known number of molecules. Thus, for the normal saturated fatty acids, no trace of surface pressure was discernible until the area per molecule was reduced to 22 sq. Å.* At 20.5 sq. Å the pressure was very marked and increased very rapidly for further decrease. It was a significant fact that these figures were not altered by using different acids provided the long-chain molecule contained a sufficient number of groups. It was this fact which led to the introduction by Langmuir of his well-known theory that such molecules are oriented into vertical or nearly vertical positions in the surface, suggesting that the sectional area of such a molecule is about 20 sq. Å. As the volume of a CH_2 group is known to be about 29 cubic Å, this gives 1.4 Å as an approximate measure of the distance of one carbon atom from the next in the chain, a measure substantially in agreement with the results obtained by X-ray analysis. This conception illuminates the whole subject. At the end of the fatty acid or alcohol molecules there is the group OH or COOH which is very soluble in water. This group tends to get into the body of the water, and although not able to drag the whole of a very long molecule in also, it succeeds in "anchoring" the molecule as it were in an almost upright position. In this oriented state the molecules adhere laterally, and this adhesion keeps them together as a "coherent" film showing no sign of surface pressure as soon as each molecule has about 22 sq. Å room for its cross section. Thus there are "condensed" films close-packed and strongly adhering, and "liquid-expanded" films in which adhesion and packing are less marked. In addition Langmuir found that certain films such as those of the short-chain fatty acids were quite different in behavior; these appear to lie flat on the surface—the argument has been given earlier in connection with statistical considerations—and to move about independently, resembling a two-dimensional gas. Such "gaseous films" appear to exert a pressure, by reason of a bombardment on the barrier due to thermal movement, entirely analogous to the three-dimensional pressure of an ordinary gas. Just as there are no "ideal" gases so there are no "ideal" gaseous films; nevertheless the laws which have been discovered to hold between the surface pressure of a given amount of gaseous film and the surface area over which it extends resemble in form the laws for gases, such as Amagat's and van der Waals'. Actually there appear to be processes in the surface analogous to fusion and vaporization and a whole new "two-dimensional" world seems to be opening up.

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* 1 Å (1 Ångstrom unit of length) = 10^{-8} cm.

So far these remarks have been concerned with films of insoluble or nearly insoluble materials, and have had no direct connection with adsorption from solutions, but in the paper already cited Langmuir used Gibbs' equation to indicate that similar conditions exist in adsorbed films. By using Szyszkowski's data on the relation between surface tension and concentration he calculated from the adsorption equation the amount adsorbed and thus obtained the area per molecule in the film for various bulk concentrations of the solutions of the very short-chain fatty acids, from 3 to 6 carbons in length. He found that with increasing bulk concentrations this tended to decrease to a constant value roughly consistent with what might be regarded as the sectional area of the molecule, thus suggesting that at the limit of adsorption there exists a close-packed unimolecular film in the surface. For the most dilute concentrations the film is, of course, much more sparsely occupied by the adsorbed solute molecules, and these appear to have the properties of a gaseous film. This is easily shown from the Szyszkowski formula

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log\left(1 + \frac{c}{a}\right).$$

Langmuir, interpreting $\sigma_0 - \sigma$ as the "surface pressure" (actually Traube suggested this interpretation for the lowering of surface tension in these adsorption films long ago), writes it

$$\begin{aligned} F &= \sigma_0 b \log\left(1 + \frac{c}{a}\right) \\ &= \sigma_0 b \left\{\frac{c}{a} - \frac{1}{2}\frac{c^2}{a^2} + \frac{1}{3}\frac{c^3}{a^3} - \text{etc.}\right\}. \end{aligned}$$

If c is small compared to a

$$F = \frac{\sigma_0 b}{a} c.$$

But

$$\Gamma = -\frac{c}{Rt}\frac{d\sigma}{dc} = \frac{\sigma_0 b}{Rt}\frac{c}{c+a}$$

or, approximately,

$$\Gamma = \frac{\sigma_0 b}{Rt}\frac{c}{a} = \frac{F}{Rt}.$$

If A is the area occupied by unit mass of the adsorbed solute then

$$FA = Rt,$$

since $A = \Gamma^{-1}$. The analogy between this and the Boyle-Charles law is obvious, and exactly the same equation can be obtained by applying to this two dimensional phase the familiar kinetic argument which derives that law for a three-dimensional gas. These gaseous films, however, deviate in practice from such an ideal law in the case of larger concentrations for which the approximations used above are no longer valid. Actually the deviations resemble the deviations for gases. Thus

$$\frac{Rt}{A} = Rt\Gamma = -\frac{d\sigma}{dc} = c\frac{dF}{dc}.$$

Therefore

$$\frac{Rt}{FA} = \frac{d\log F}{d\log c}$$

or

$$\frac{FA}{Rt} = \frac{d\log c}{d\log F}.$$

From the tables of c and F (or $\sigma_0 - \sigma$), the values of FA/Rt for various concentrations can be calculated and plotted against F. The curves show a resemblance to the $(PV/Rt, P)$ curves for gases. (See Rideal's *Surface Chemistry*, Chapter II, page 65.) Indeed an equation analogous to Amagat's has been shown by Schofield and Rideal (ibid., page 66) to represent with some exactitude the behavior for all but the most dilute concentrations. It is

$$F(A - B) = xRt,$$

where B is the limiting area of the unit mass of molecules when crowded together in the unimolecular film, and x is a measure of the lateral molecular cohesion, having a definite value not greater than unity for each solute, and being smaller the larger the cohesion. The values of B agree quite well with the values suggested from other considerations. The equation is well supported by its application to about a dozen solutes which include the shorter-chain fatty acids and some alcohols. In so far as it is valid it leads to an interesting equation as follows. By the exact Gibbs' equation

$$dF = - d\sigma = \Gamma d\mu .$$

Therefore

$$\frac{d\mu}{dF} = \Gamma^{-1} = A$$

$$= B + xRt \cdot \frac{1}{F} .$$

Integrating,

$$\mu = BF + xRt \log F + \text{constant}.$$

If a is the activity of the solute

$$Rt \log a = xRt \log F + BF + \text{constant}$$

and so

$$a = CF^x \exp\left(\frac{FB}{Rt}\right).$$

Rideal states that this equation is in good accord with the precise surface tension measurements of Szyszkowski. A two-dimensional analogue of van der Waals' equation has also been suggested, but data do not appear to be available over a wide enough range of temperature to justify a definite opinion.

26. Unimolecular Layers and the Dividing Surface

This use of Gibbs' equation and the consistency of the information which it gives concerning the surface structure, is strong evidence for its validity in the case of substances such as the shorter-chain fatty acids. Indeed, this conception of the unimolecular Gibbs layer may throw some light on the discrepancies which have raised doubt concerning its validity. There does not appear to have been any such idea in Gibbs' own mind. Possibly he held the view which, with the weight of Laplace's name behind it, seems to have been prevalent in his day, viz., that the discontinuous layer, although physically very thin, is nevertheless many molecules thick and shows a gradation of properties as it is passed through. Yet if the layer is really only a molecule or two thick, the placing of the dividing surface becomes a somewhat perplexing matter. Indeed, the whole physical theory of placing the "surface of tension" so as to exclude the $C_1 \, \delta c_1 + C_2 \, \delta c_2$ terms in the original differential equation becomes very doubtful. Earlier in this commentary we have somewhat expanded Gibbs' presentation of this in order to assist the reader to an understanding of his concise formulation, and on referring to this again the reader will see that the basis of it is hardly tenable for a unimolecular layer. A very significant illustration of the point involved here will be found in two well-known calculations made by Schofield and Rideal (*Proc. Roy. Soc.*, **109 A**, 57, (1925)); they refer to alcohol and pyridine. The data for the surface tension of mixtures of water and ethyl alcohol from pure water to pure alcohol were known from some work of Bircumshaw, and data for the partial vapor pressure of ethyl alcohol could also be obtained so as to give the activity and therefore the potential. With the aid of these the surface excess of alcohol was calculated by the strict Gibbs' equation for over a dozen mixtures between the extreme limits. It was found that this excess rose very rapidly until it attained a maximum when the mol fraction of the alcohol was about 0.25, and the value there corresponded to an area of 24 sq. Å per alcohol molecule, which indicates a close-packed unimolecular layer of these molecules. Thereafter the surface excess rapidly fell, and when the mol fraction was 0.75 the surface excess was apparently no greater than it was when the mol fraction had a value well under 0.1; this value of surface excess was apparently maintained for mixtures still richer in alcohol right up to alcohol itself. Exactly similar results were obtained for the surface excess of pyridine at the interface between mercury and mixtures of pyridine and water, care being taken to neutralize the electric charge which is known to exist normally at a surface between mercury and water. Now it is highly improbable that there is really a decrease in the surface excess with increase in the proportion of alcohol or pyridine, and the situation shows how troublesome the interpretation of Gibbs' equation may become in particular cases. We have seen that it does definitely point to the existence of a unimolecular layer, and there is also evidence, which we shall touch on later in this commentary, that at least partial orientation of the molecules occurs as well (just as in the case of insoluble films). Now it might happen that with increasing concentration of the alcohol, the more polar water molecules being replaced by weaker alcohol molecules, there would be a decrease in orientation with an increase in area occupied, caused by each alcohol molecule lying flatter in the surface. But a more probable explanation has been given by Rideal and Schofield, viz., that there is formed below the outer layer of alcohol, a second layer of water. "In the derivation of Gibbs' equation, the mathematical dividing membrane *XY* was so placed as to make the adsorption of the water zero—that is, so that the average concentration of water in volumes above and below *XY* were exactly equal to those in the vapor and the liquid at a distance from the surface. If there is a layer of water below the outermost layer of pure alcohol, this will involve placing the dividing surface, not below the alcohol molecules, but some distance above the average level of their lowest points, perhaps more than half-way up the molecules (owing to the thermal agitation this refers to the *average position* of the alcohol molecules)."* As the alcohol in the bulk phase is supposed also to extend up to this dividing surface with the bulk concentration, *for the purpose of calculating* Γ *for the alcohol,* such a gradual creeping outward of the surface will have the effect of causing only a portion of the outer layer of alcohol molecules to appear as "adsorbed alcohol." This illustrates very forcibly the difficulties that arise when we begin to "tamper" with the dividing surface for the purpose of getting rid of a term in the true adsorption equation for a binary mixture, viz., (at constant temperature)

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2.$$

If, however, we keep the dividing surface fixed, say at the depth of the unimolecular layer, we can use the equation referred to earlier,

$$\frac{d\sigma}{d\mu_2} = -\left(\Gamma_2 - \Gamma_1 \frac{\gamma_2'}{\gamma_1'}\right),$$

(the equation [515] of Gibbs, slightly modified). This incidentally shows us how the right-hand side of the equation diminishes with increasing alcohol concentration; for with an accumulation of water molecules in the layer just inside the *fixed* dividing surface, Γ_1 is positive and increasing and γ_2'/γ_1' is also increasing in the bulk phase. This is then a way of stating the explanation, alternative to that using the moving surface. It has been suggested by Bradley (*Phil. Mag.*, **7**, 142, (1929)) that an additional relation, which with the above would enable us to determine both Γ_1 and Γ_2 could be obtained from the alteration in the air-liquid electric potential difference which is dependent on the electric moments of solvent and solute molecules in the surface layer; this would of course change with the change in the composition of the surface. The reader is referred to this paper for further information.

The difficulty of the situation is clear, and it is possible that similar considerations may be brought to bear on all the apparent failures of the Gibbs law. Unfortunately it is not easy to see how this can be done in connection with the work of McBain and his colleagues. There the difficulty is different from that just dealt with. The experiments on amyl alcohol, for example, show that the measured amount at maximum adsorption was so great that if it were packed in a unimolecular layer the area was only 14 sq. Å for each molecule; in the case of sodium oleate only 11 sq. Å. It is impossible for these molecules to be packed so tightly in a layer one molecule thick. It may be possible, as we have stated earlier, that there may be a unimolecular layer with the additional material forced out into small droplets above it here and there, the unimolecular layer being the true adsorption agreeing with the adsorption equation. But clearly these difficulties still await solution. It is interesting to note that a somewhat similar situation exists in connection with insoluble oil films. The evidence for unimolecular layers is strong, yet there can be no doubt that the area of an oil film can be reduced until there is no longer room for all the molecules at their closest possible packing. The suggestion is that the film gives way under tangential squeezing, buckles and expels enormous numbers of molecules to form local ridges, the rest of the film being unchanged. Adam in his book hazards the opinion that the cases of "polymolecular" films such as those obtained by Harkins and Morgan (*Proc. Nat. Ac. Sci.*, **11**, 637, (1925)) are really examples of "partially collapsed unimolecular films, with the excess material collected into lumps much thicker than the film itself."

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* Quoted from Adam's book, p. 131.

X. Desorption

27. Unimolecular Layers and Negative Adsorption

If a solute raises the surface tension of a solution above that of the pure solvent, the Gibbs' equation shows that the calculated value of Γ_2 (Γ_1 being made zero as usual) is negative. This is interpreted by saying that the surface is poorer in the solute than the bulk phase or (alternatively) richer in the solvent. In the nature of things "negative adsorption" cannot reach such large *numerical* values as the positive; obviously it cannot exceed the bulk concentration of the solute divided by the thickness of the layer in numerical amount.*

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* See Gibbs, I, 274.

The data available are not numerous, and concern aqueous solutions of familiar inorganic salts such as the chlorides, nitrates and sulphates of familiar metals. A table of results will be found on page 74 of Rideal's book; these indicate that for a given salt the increase in surface tension above that of water varies in an approximately linear manner with the salt concentration. Langmuir has considered these results also from the point of view of a unimolecular layer. The quantity of solute which has gone out of the surface film so as to leave it poorer in the solute than a corresponding volume of solution is $c\zeta$ per unit area (where c is bulk concentration and ζ the film thickness) *if a film of pure water one molecule thick* exists at the surface. Hence on this hypothesis $c\zeta$ should equal $-\Gamma$ obtained by the equation

$$\begin{aligned}\Gamma &= -\,c\frac{d\sigma}{dc}\\ &= -\,c\frac{d(kc)}{dc}\\ &= -\,kc\,,\end{aligned}$$

since, as we have stated, $\sigma_0 - \sigma$ is approximately equal to $-kc$, where k is a constant. Hence ζ can be calculated. This should be the thickness of an adsorbed *water* layer on the surface. Langmuir found ζ to be from 3.3 to 4.2 Å, which is certainly the right order of magnitude for a water molecule if it is not of an elongated shape. More recent work by Goard, Harkins and others, using the accurate form of Gibbs equation, finds varying values for ζ which decrease from Langmuir's value between 4 and 5 Å at low bulk concentrations to about 2.5 Å at high concentrations. Adam suggests that this diminution may be due to the increasing tendency of the solute to diffuse into the surface layer as the bulk concentration increases.

The evidence for the truth of Gibbs' law in connection with the hypothesis of unimolecular layers is imposing, and one further remark may be made with reference to the cases of apparent failure in the attempts to verify it by direct measurements.

It has already been stated that recent research shows the existence in the case of numerous substances of surface films in different phases, liquid, solid, gaseous, which can occur under stable conditions at definite temperatures. If this is so the surface layer may not always be a *single* phase of the whole system; we may have at times to consider it as a system of phases and treat them thermodynamically just as we treat the different homogeneous bulk phases. The usual procedure would show that the potential of each component would have the same value in each surface phase, still agreeing with the value of this component in each of the homogeneous bulk phases. Actually, in the subsection of Gibbs' treatise which deals with the stability of surfaces of discontinuity, he considers the possibility of a part of the surface being changed in nature while the remaining part remains as before, and the entropy, total masses and volumes of the whole system remain unchanged. The changed part is to be uniform in nature and still to be in equilibrium with the adjacent bulk phases. We shall comment on this presently; but in the meantime we may anticipate and mention the conclusion to which Gibbs comes (page 240). If two films of the same components can exist between the same homogeneous masses, having the same temperature and potentials as the homogeneous masses have for the components in those masses, and the same potentials for components only existing in the surface, then the film which is most stable is the one with the smaller tension. Consequently in a *stable* film consisting of two or more surface phases the surface tension for each must be the same, for if one phase had a greater surface tension than the other it would disappear on the slightest disturbance of equilibrium. Suppose, therefore, that with increasing bulk concentration there comes a point when a part of a hitherto gaseous film begins to condense into a liquid film. This seems to be a natural way of imagining the creation of a close-packed unimolecular layer. A small addition of the solute to the bulk phase would not result in an increase of bulk concentration; all the material would go to the surface gradually increasing the extent of the liquid surface phase which encroaches on the gaseous; during this period there would be no increase of σ or of the potential of the solute. Supposing now that σ_a is the value of the surface tension and μ_{2a} the value of the potential of the solute at a concentration below this transformation point, and σ_b and μ_{2b} values above it, then $(\sigma_a - \sigma_b)/(\mu_{2b} - \mu_{2a})$ would be intermediate in value between the surface concentration of the gaseous film and that of the liquid film. The essential point is that it would be less than the actual concentration in the liquid film. This is a somewhat enlarged version of an explanation suggested by Rideal in his book, on pages 51 and 52, to account for the fact that Γ observed is nearly always greater than Γ calculated.

28. The Recent Experiments of McBain and Humphreys on Slicing Off a Thin Layer at a Surface

Note: Just as this manuscript is going to press the writer has read in the *Journal of Physical Chemistry*, **36**, 300 (1932), a preliminary account by McBain and Humphreys of some fresh experiments in progress on the determination of the absolute amount of adsorption at surfaces of solutions, and if subsequent results follow the indications given by these then it may be said that very dependable evidence for the truth of Gibbs' law by direct measurement is at last available. The apparatus is extremely ingenious, and is novel in that for the first time a *static* surface is involved and not one which is in motion, as in the experiments with bubbles; the criticisms levelled against the latter have been referred to above.

Briefly, the solution is at rest in a shallow trough of silver surrounded by a saturated atmosphere. The ends of the trough are paraffined, so that the solution is made to bulge up above them without overflowing. A uniform layer 0.05 to 0.1 mm. thick is cut off from a known area of the surface by a small microtome blade travelling at a speed about 35 feet per second. This layer is collected in a small silver-lined cylinder, on which the blade is mounted, and is weighed, its concentration being then compared with that of the bulk solution by means of a Lewis interferometer. From the observed difference of concentration the adsorption can be calculated. Extraordinary precautions appear to have been taken against every conceivable source of error.

The following results of preliminary trials indicate the very satisfactory agreement now obtained between Γ calculated and observed. It is no longer a matter of agreement of order of magnitude, or a ratio between 2:1 and 4:1.

Substance	Concentration (grams per 1000 grams H_2O)	$\Gamma \times 10^8$ obs.	$\Gamma \times 10^8$ calc.
p-Toluidine	2.00	6.1	5.2
p-Toluidine	1.76	4.6	4.9
Phenol	20.48	4.1	4.8
Caproic Acid	2.59	6.8	6.3
Caproic Acid	3.00	5.1	6.5
Caproic Acid	5.25	6.2	6.3
Hydrocinnamic Acid	1.5	5.6	5.1
Hydrocinnamic Acid	4.5	5.4	7.9

XI. Adsorption of Gases and Vapors on Liquid Surfaces

29. Form of Gibbs' Equation for Adsorption from a Gaseous Phase

Hitherto we have considered the experimental tests on adsorption from the liquid side of a gas-liquid interface; but we must make some reference to the work carried out on adsorption from the other side. In such experiments it is convenient to replace the potential of the gaseous component by its pressure in the adsorption equation. The theory of such transformation of variables is given very completely by Gibbs (I, 264–269). For our purpose we need only consider the part on pages 267–268 which leads to equation [581]. We shall suppose that the single accent phase is the liquid, the double accent the gaseous, that component 1 is the liquid, and component 2 the gas or vapor adsorbed. From equation [581] we see that if σ is regarded as a function of the temperature and pressure, then

$$\frac{\partial \sigma}{\partial p} = \frac{C}{A},$$

where C and A are given at the top of page 268. Now γ_1' is the density of the liquid and γ_1'' is the density of the liquid's vapor in the gaseous phase, so that γ_1'' is very much smaller than γ_1'; γ_2'' is the density of the gas or vapor, whose adsorption is being considered, in the gaseous phase; γ_2' its density in the liquid bulk phase, may be regarded as zero. Hence, practically,

$$\begin{aligned} A &= -\gamma_1'\gamma_2'', \\ C &= \Gamma_1\gamma_2'' + \Gamma_2(\gamma_1' - \gamma_1'') \\ &= \Gamma_1\gamma_2'' + \Gamma_2\gamma_1' . \end{aligned}$$

Therefore

$$\frac{C}{A} = -\frac{\Gamma_1}{\gamma_1'} - \frac{\Gamma_2}{\gamma_2''} .$$

Since Γ_1 is zero by the choice of dividing surface, it follows that

$$\frac{C}{A} = -\frac{\Gamma_2}{\gamma_2''}$$

or

$$\Gamma_2 = -\gamma\frac{\partial\sigma}{\partial p},$$

where γ refers to the density of the adsorbed vapor in the gaseous phase.* Before passing on to consider the experimental results we may remind the reader of the mechanical explanation of gaseous adsorption given in the last paragraph of section IV of this article. The existence of a surface energy depends, as we saw, on a normal field of force existing in a molecular layer at the surface of the liquid and also extending a similar distance into the space above the liquid. Such a field would cause an increased concentration of gas close to the surface, just as the density of the atmosphere is greatest at the lowest level in the earth's gravitational field. Actually the outward attraction of this concentrated layer of gas would tend to weaken the field of force to which it is due and so produce a diminution in the surface energy.

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* Not of the liquid's vapor; γ_1'' is the density of that.

30. The Experiments of Iredale

We shall first briefly review the results obtained in Donnan's Laboratory by Iredale (*Phil. Mag.*, **45**, 1088 (1923); **48**, 177 (1924); **49**, 603 (1925)). He deals principally with the adsorption of vapors of organic substances at the surface of mercury; these have the property of lowering the surface tension of mercury. The drop weight method of determining surface tension was used and its accuracy is carefully discussed. The vapors were generated by passing a very slow current of dry air at constant pressure through the organic liquids. The adsorption of the vapor at the surface of the drops appeared to be a fairly rapid process; for "the period of drop formation was never less than $3\frac{1}{2}$ minutes and with longer periods the weights of the drops were not found to decrease appreciably" thus indicating that a steady condition of surface tension had been reached. The results with methyl acetate vapor showed a fall from 470 dyne per cm. to about 430 for a partial pressure of 40 mm. in the vapor; thereafter the fall was much slower, reaching a value about 412 dynes as saturation of the vapor at about 225 mm. was approached. At this point there was a sudden fall of the surface tension to about 370 dynes which is the value of the surface tension of mercury in liquid methyl acetate. Taking the slope of the graph, which gives $d\sigma/dp$ at 62 mm. pressure, where the conditions of maximum adsorption are being approached although the vapor pressure is still well away from saturation, and multiplying it by γ for the vapor there, a value about 4.5×10^{-8} gram of methyl acetate per sq. cm. is obtained. This corresponds to about 0.37×10^{15} methyl acetate molecules per sq. cm. of mercury surface. This figure is near the values given by Langmuir (*J. Am. Chem. Soc.*, **38**, 2288, (1916)) for unimolecular layers of carbon dioxide, nitrogen, etc. "Moreover the space taken up by each molecule (27×10^{-16} sq. cm.) is near that required for molecules of esters and fatty acids on the surface of water, namely, 23×10^{-6} sq. cm., and it is possible that the same type of orientation obtains on the mercury surface.

There appears, however, to be a somewhat abrupt change from a simple adsorption process to a condensation." In later work Iredale examined more carefully the remarkable behavior exhibited at the saturation point of the vapor. Among the vapors studied was water vapor in the presence of air. In this case the slope of the (σ, p) curve was practically uniform up to the saturation point, and so the adsorption increased uniformly with the density and partial pressure of the vapor right up to the saturation point. Calculation of Γ at this point gives a value 1.8×10^{-8} gram per sq. cm. which is somewhat less than that required for a unimolecular film (3.8×10^{-8} gram per sq. cm. according to Langmuir). At the saturation point there is the same instability in the tension of the vapor-mercury interface, its value being entirely uncontrollable and lying anywhere between 447 and 368 dynes per cm. Iredale suggests that the primary phenomenon is the gradual formation of a unimolecular layer, this being represented by the earlier portion of the curve. After the vapor reaches the saturation value a very thin film of liquid may be produced, the thickness of which "is not a determinate function of the pressure and temperature, though the most stable state corresponds to the formation of a film, which may, from the standpoint of intermolecular forces, be regarded as infinitely thick." Iredale also examined the adsorption of benzene vapor on a mercury surface. This showed one rather unexpected feature. He considered that near the saturation point the value of Γ attained a maximum and decreased slightly with a further small increase of pressure. He also found a similar tendency in methyl acetate, though not in water vapor. (This was criticized later by Micheli whose work we shall refer to presently.) The maximum value for benzene was such as agreed with an area 21×10^{-16} sq. cm. for each molecule, very near to Adam's value (23.8×10^{-16}) for certain benzene derivatives on a water surface, and once more supported the view that the vapors adsorbed on the surface of mercury tend to form primary unimolecular films. Further measurements were made using the sessile drop method for measuring surface tension, and without admixture of air. These results were in fair agreement with the previous work and gave much the same value for the area per molecule of adsorbed benzene on the mercury surface. Experiments were carried out with ethyl alcohol, propyl chloride, and ethyl bromide, showing that, as in the previous cases, the adsorption of these substances appears to be within certain limits a reversible phenomenon. Iredale expresses surprise that these substances, "which are more definitely polar than benzene and, especially in the case of the alkyl halides, possess an atom or group more likely to form a definite linking at the mercury surface, should have no more marked effect on the surface tension than benzene itself."

31. *The Experiments of Micheli, Oliphant, and Cassel*

Subsequently Micheli at Donnan's suggestion (*Phil. Mag.*, **3**, 895 (1927)) took up the same problem. He examined the vapors of benzene, hexane, heptane, pentane and octane, all in a high state of purity, at a water-vapor interface using the drop-weight method. It was found that if σ is plotted against the partial pressure of the vapor (in the vapor-air mixture) the result is a straight line; hence $\Gamma = kP$, where k is a constant. From a knowledge of k, Γ_s the amount adsorbed when the partial pressure is equal to the maximum vapor pressure at the temperature of adsorption could be determined. His comment on the results is as follows: "The fact that a linear relationship holds between the partial pressure of the vapor and Γ right up to the value Γ_s, and also that this quantity changes so rapidly with increasing temperature, indicate clearly that a limiting condition, such as would obtain if a closely-packed adsorbed layer were formed, had not been reached." He also shows from his calculations that the values for the area occupied by one molecule of benzene is larger than Adam's value for a closely packed layer of certain benzene derivatives on a water surface. "In this case, clearly an unsaturated layer is formed." His proportionality factor decreases as the temperature at which the experiments are performed is raised. This indicates that adsorption is accompanied by an evolution of heat, but we shall postpone the discussion of this matter until we reach the commentary on the subsection dealing with thermal effects.

This work was carried out at a water surface. However, Micheli also experimented with a mercury-air interface, substantially confirming Iredale's conclusion that at this surface the amount adsorbed approaches a definite limiting value as the partial pressure of the hydrocarbon vapor increases, and that the values of the area per molecule obtained from Γ_s in this case agreed well with Adam's value for benzene already referred to and, in the case of pentane, hexane, heptane and octane, with the values also found by Adam for closely packed molecules of straight-chain alphatic acids or alcohols oriented at a water-air interface so that the OH or COOH groups are attached to the surface. One feature of Iredale's work with benzene, Micheli did not obtain; this concerned the point of inflexion obtained by Iredale on his (σ, log p) curve for benzene, indicating a maximum adsorption before saturation was reached, with a subsequent diminution. Micheli remarks that such an effect would not be probable, and draws attention to the curves of Schofield and Rideal concerning the adsorption of ethyl alcohol from an aqueous solution on which we have already commented and where a similar *apparent* maximum exhibits itself. Micheli states that the observed maxima really indicate that conditions exist which render the Gibbs equation inapplicable, and is obviously suggesting that we must look for an explanation of Iredale's result, if it really exists, along the lines already referred to in our previous comments on this point.

It is interesting to observe that Gibbs' own footnote on page 235 is concerned with adsorption from a vapor phase. He quotes some figures of Quincke for the tension of mercury in contact with air (which he takes to be practically the same as for contact with its own vapor free of water vapor), and for the interfacial tension of water and mercury and of water and its vapor. They are, when expressed in present-day units, 539, 417 and 81 dynes per cm. Assuming that the tension of mercury in contact with the *saturated vapor* of water is the sum of the two latter, which is tantamount to assuming that at saturation pressure of water vapor the adsorbed film is beginning to have the properties of *water condensed in mass*, the reduction in the tension of mercury by adsorption of water vapor is 41 dynes per cm. for an increase of water vapor pressure of 1.75 cms. of mercury. There he leaves the calculation, but had he known, as we know now from Iredale's and Micheli's work, that the fall in tension is proportional to the increase of vapor pressure, he could have finished the calculation for the amount of the layer adsorbed just at saturation before actual condensation into a genuine liquid water phase begins. For

$$\frac{d\sigma}{dp} = \frac{-41}{1.75 \times 981 \times 13.6},$$

and

$$\Gamma = -\gamma \frac{d\sigma}{dp} = \frac{17.4 \times 10^{-6} \times 41}{1.75 \times 981 \times 13.6}$$
$$= 3 \times 10^{-8} \text{ (grams per sq. cm.)},$$

since γ, the density of water vapor at 20°C, is 17.4×10^{-6} grams per c.c. This is just the figure for a unimolecular film of water molecules, but there is no doubt that no such conception was in his mind. Indeed, the assumption he makes above shows this. Iredale in one of his papers has some very interesting remarks to make on the general theory of adsorption and condensation, but reference to them will be deferred until we have commented on the subsection of Gibbs' work which deals with the formation of a new phase at the interface between two phases, since Iredale's comments involve the theoretical considerations in that subsection.

Another very interesting set of experiments were carried out by Oliphant (*Phil. Mag.*, **6**, 422, (1928)). His apparatus was adapted from one invented for another purpose by Schofield. He found that an expanding mercury surface selectively adsorbs carbon dioxide from a mixture of that gas with an excess of hydrogen or argon, and that at all concentrations above 2 per cent the carbon dioxide thus selectively adsorbed was constant at a value about 6.5×10^{14} molecules per sq. cm. This very nearly corresponds to a close-packed unimolecular layer. Actually, Schofield's method does not involve the $\gamma\partial\sigma/\partial p$ rule or the measurement of $\partial\sigma/\partial p$. It should be mentioned that

Bircumshaw (*Phil. Mag.*, **6**, 510, (1928)) has found that the surface tension of mercury in contact with such gases exhibits some anomalies with lapse of time which have not yet been explained. Finally, reference should be made here to the excellent work of H. Cassel and his collaborators on the adsorption of gases and vapors on mercury and water surfaces (*Z. Elektrochem.* **37,** 642 (1931); *Z. physik. Chem., Abt. A*, **155,** 321 (1931); *Trans. Faraday Soc.*, **28,** 177 (1932); *Kolloid-Z.*, **61,** 18 (1932)).

XII. The Thermal and Mechanical Relations Pertaining to the Extension of a Surface of Discontinuity

32. *Need for Unambiguous Specification of the Quantities Which Are Chosen as Independent Variables*

In this subsection Gibbs makes use of the results obtained in the previous subsection of his work, to which we have already referred at the beginning of the part of the commentary just concluded. The results are in equations [578], [580] and [581]. When there is one component in two homogeneous phases and a surface of discontinuity, σ is a function of t and μ (the one potential involved). The transformation effected at the bottom of page 265 still leaves it a function of two variables t and $p' - p''$. If the surface is plane there is only one variable, t, involved; this is obvious in any case since with only one component in two phases, say vapor and liquid, p is a function of t, and of course σ is also.

Equation [580], which refers to *two* components in two homogeneous phases, and equation [581] are framed as if σ were again a function of two variables, and yet σ is originally regarded as a function of three, viz., t and the potentials μ_1 and μ_2 of each component. The reason is clear. Equation [579] shows that there are really three variables involved, t and the two pressures; but since the surface is regarded as practically plane, the difference between the two pressures is ignored. Actually, since the surface is plane and $p' = p''$, this gives us an equation between two functions of t, μ_1, μ_2 and thus μ_2 is a function of t and μ_1 and is not an independent variable; so σ is really a function of t and μ_1 or t and p. It would be a great assistance to students of thermodynamic texts if writers would cultivate the habit of indicating by bracketed symbols just what quantities are being considered as the variables upon which the physical properties being discussed are dependent,—at all events in circumstances where ambiguity might otherwise easily arise. For example, in the present instance, σ regarded as depending on t, μ_1, would be written as $\sigma(t, \mu_1)$, meaning the function of the variables t, μ_1 which is, for any given values of t and μ_1, equal to the value of the surface tension at these values of temperature and the potential of the first component. On the other hand σ regarded as depending on t, p would be written as $\sigma(t, p)$. Of course it would be implied in such a convention that the *functional form* of $\sigma(t, \mu_1)$ would not be the same as $\sigma(t, p)$. Actually, to satisfy the requirements of a strictly rigorous use of mathematical symbolism we should write the two functions, which both represent the same physical quantity, in different ways, say $f(t, \mu_1)$ and $g(t, p)$; but the situation does not really demand such rigor and there is an advantage in indicating just what physical quantity is being represented, provided the implication referred to is kept in mind. Such a symbolism when combined with the modern *partial* differential coefficient notation (the use of ∂ instead of d, not in use when Gibbs wrote his memoir), would also clearly indicate what quantities are being regarded as constant in any particular differentiation, so that the use of the subscript after a bracket (the usual method of the thermodynamic texts) would be unnecessary. Thus in equation [593] $(d\sigma/dt)_p$ would be $\partial\sigma(t, p)/\partial t$ and $(d\sigma/dp)_t$ in [595] would be $\partial\sigma(t, p)/\partial p$. In [587] and [592] the differentials are total differential coefficients. Gibbs makes a special reference to this point at the top of page 271. With only *one* component, say a liquid and its vapor, p is a function of t, and σ can be regarded either as a function of p only or as a function of t only and written accordingly $\sigma(p)$ or $\sigma(t)$ as the case may be; so that in [587] the *total* differential coefficient symbol would still be correct and we would write it as

$$Q = -t\,\frac{d\sigma(t)}{dt}\,.$$

In [592] p is a function of t, and so t is a function of p and we have

$$W = -p\frac{d\sigma(t)}{dt} \cdot \frac{dt(p)}{dp},$$

and the right hand side by a well-known proposition of the differential calculus is equal to

$$-p\frac{d\sigma(p)}{dp}.$$

The reader whose acquaintance with mathematical technique may be limited should not regard these remarks as idle comments on mere mathematical "niceties." Actually, if the method suggested were more widely used, and not merely in thermodynamic texts, it would conduce to clarity of exposition and consequent ease of understanding on the part of the reader.

33. Alternative Method of Obtaining the Results in This Section. Total Surface Energy

The methods by which Gibbs arrives at the results of this section are easy to follow and eminently physical. It may not be out of place, however, to obtain them by a more analytical method which will also help to illustrate the remarks just made.

Thus the energy of the *whole* system consisting of two phases and surface of discontinuity with n components is a function of the variables η, v, s, m_1, m_2, ... m_n, since

$$\epsilon = t\eta - pv + \sigma s + \mu_1 m_1 + \mu_2 m_2 \ldots + \mu_n m_n{}^*$$

and

$$d\epsilon = td\eta - pdv + \sigma ds + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n.$$

We should write the functional form which represents the energy in these variables as $\epsilon(\eta, v, s, m_1, m_2, \ldots)$ but actually, with the assumption of a practically plane interface, we have an equation

$$p'(t, \mu_1, \mu_2, \ldots) = p''(t, \mu_1, \mu_2, \ldots).$$

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* See Gibbs, I, 240.

This gives us one equation between the variables and so we can reduce them from $n + 3$ in number to $n + 2$; the most convenient set of variables is then $\eta, v, s, r_1, r_2, \ldots r_{n-1}$, where $r_1 = m_1/m_n$, $r_2 = m_2/m_n$, etc. So we write the function for ϵ as $\epsilon(\eta; v, s, r_1, r_2, \ldots)$ and

$$d\epsilon(\eta, v, s, r_1 r_2, \ldots) = td\eta - pdv + \sigma ds + \nu_1 dr_1 + \nu_2 dr_2 + \ldots,$$

where ν_1, ν_2, etc. are functions of $\eta, v, s, r_1, r_2, \ldots$

The other three Gibbs functions are then

$$\begin{aligned} \psi(t, v, s, r_1, r_2, \ldots) &= \epsilon - t\eta, \\ \zeta(t, p, s, r_1, r_2, \ldots) &= \epsilon - t\eta + pv, \\ \chi(\eta, p, s, r_1, r_2, \ldots) &= \epsilon + pv, \end{aligned}$$

with the differential equations

$$\left.\begin{aligned} d\psi(t, v, s, r_1, r_2, \ldots) &= -\eta dt - pdv \\ &\quad + \sigma ds + \nu_1 dr_1 + \ldots, \\ d\zeta(t, p, s, r_1, r_2, \ldots) &= -\eta dt + vdp \\ &\quad + \sigma ds + \nu_1 dr_1 + \ldots, \\ d\chi(\eta, p, s, r_1, r_2, \ldots) &= td\eta + vdp \\ &\quad + \sigma ds + \nu_1 dr_1 + \ldots \end{aligned}\right\} \tag{22}$$

From the second of those we have

$$\frac{\partial\zeta(t, p, s, r_1, r_2, \ldots)}{\partial t} = -\eta(t, p, s, r_1, r_2, \ldots)$$

and

$$\frac{\partial\zeta(t, p, s, r_1, r_2, \ldots)}{\partial s} = \sigma(t, p, s, r_1, r_2, \ldots)^*.$$

By cross differentiation

$$\frac{\partial\eta(t, p, s, r_1, r_2, \ldots)}{\partial s} = -\frac{\partial\sigma(t, p, s, r_1, r_2, \ldots)}{\partial t}.$$

---

* Actually σ is only dependent on t, p and $n - 2$ of the ratios $r_1, r_2, \ldots$

This is equation [593]; the left-hand side is the rate of change of entropy with increase of surface, while t, p and the composition of the masses are unchanged (this is the condition stated in the paragraph preceding [593] in Gibbs), and so is equal to Q/t. In the right hand side the variables p, r_1, r_2, ... are kept unchanged in the differentiation; in Gibbs' case no ratios occur in the variables on which σ depends, since he is dealing with two components only and there would only be one ratio r, and even this does not appear since we have just stated in the footnote that in general σ depends on only $n - 2$ of the $n - 1$ ratios r_1, r_2, ... as well as t and p. Indeed σ depends only on n variables; for we know it can be expressed as a function of t, μ_1, μ_2, ... μ_n in general, but the assumption of the equality of pressures in the two phases reduces the number of variables to n.

The addition of Q to σ gives the total energy acquired by the surface when extended one unit of area if the temperature, pressure and composition of the phases remain unchanged. This quantity

$$\sigma(t, p, r) - t\frac{\partial\sigma(t, p, r)^*}{\partial t}.$$

is sometimes called the total surface energy, σ being called the free surface energy. With the exception of a few molten metals, liquids exhibit a decreasing surface tension with rising temperature, and so as a rule total surface energy is greater than free surface energy. In many liquids the relation between σ and t is linear, so that the total surface energy does not vary with temperature. Actually, if the variation is not zero, we can easily see that the ordinary specific heat of a liquid will vary with the extent of surface offered by a definite mass of it which will change with a change of form in the mass. For

$$\frac{\partial}{\partial t}\left\{\sigma(t, p, r) - t\frac{\partial\sigma(t, p, r)}{\partial t}\right\} = -t\frac{\partial^2\sigma(t, p, r)}{\partial t^2}$$

$$= t\frac{\partial^2\eta(t, p, s, r)}{\partial t\,\partial s} = \frac{\partial}{\partial s}t\frac{\partial\eta(t, p, s, r)}{\partial t}.$$

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* For brevity let r stand for the series r_1, r_2, ... r_{n-1}.

Now $t\partial\eta/\partial t$ is the ordinary heat capacity of the mass of the fluid, and if the left hand side of the equation is not zero, the specific heat will depend on s.

The fact that extension of the surface of a liquid (all the other variables remaining constant) involves cooling in most cases (as is obvious since, in general, heat must be supplied to maintain the temperature constant) can be seen very easily from mechanical considerations. We can imagine the system of liquid and vapor to be contained in a flexible but non-expanding enclosure which will permit a change of extent of surface without alteration in volume, etc. of the two individual phases. In enlarging the surface some molecules must pass from the interior to the surface; i.e., must travel through the molecular cushion against the inward attracting field of force there. This involves an increase of potential energy, and with no supply of energy from without there must be a diminution of molecular kinetic energy, which means a fall of temperature.

The equation [593] or the form which we have given it above can be written in another form involving the total surface energy. Thus

$$\sigma(t, p, r) - t\,\frac{\partial\sigma(t, p, r)}{\partial t} = \sigma(t, p, r) + t\,\frac{\partial\eta(t, p, s, r)}{\partial s}.$$

Also, by the third equation of (22), we see that

$$\frac{\partial\chi(t, p, s, r)}{\partial s} = t\,\frac{\partial\eta(t, p, s, r)}{\partial s} + \sigma(t, p, r),$$

where on the left-hand side we suppose that Gibbs' "heat function," χ, is expressed in terms of the variables t, p, s, r. Hence

$$\sigma(t, p, r) - t\,\frac{\partial\sigma(t, p, r)}{\partial t} = \frac{\partial\chi(t, p, s, r)}{\partial s}.$$

This will be found on careful examination to be equation 22 of Chapter XXI of Lewis and Randall's *Thermodynamics*.

The equation [594] of Gibbs can be obtained by similar methods. Thus by the second equation of (22)

$$\frac{\partial \zeta(t, p, s, r)}{\partial p} = v(t, p, s, r)^*,$$

and

$$\frac{\partial \zeta(t, p, s, r)}{\partial s} = \sigma(t, p, r).$$

Hence by cross-differentiation

$$\frac{\partial v(t, p, s, r)}{\partial s} = \frac{\partial \sigma(t, p, r)}{\partial p}.$$

The left-hand side is the quantity $-V$ in Gibbs' text. This equation also appears in Lewis and Randall's book as equation 19 of Chapter XXI.

34. Empirical Relations Connecting σ and t. Degree of Molecular Association in Liquids

We have referred above to the approximately linear relation between surface tension and temperature for many liquids. Also, since surface tension must vanish at or near the critical temperature of a liquid, the relation should then be

$$\sigma = \sigma_0 \left(1 - \frac{t}{t_c}\right),$$

where σ_0 is a constant for the liquid and t_c the critical temperature. Almost 50 years ago Eötvös from a not too rigorous argument suggested that the constant σ_0 should vary as the number of molecules in unit area of the liquid surface; since the number of molecules per unit volume varies inversely as MV, where M is the molecular weight of the liquid and V the specific volume of the liquid, σ_0 would then vary inversely as $(MV)^{\frac{2}{3}}$ or directly as $(D/M)^{\frac{2}{3}}$, where D is the density of the liquid. About ten years later Ramsay and Shields, in a series of well-known researches, found considerable support for the law provided M was taken to be the molecular weight of the *liquid* and not of the vapor. Indeed this work was used to calculate the degree of association in many liquids. Ramsay and Shields actually made another slight modification of Eötvös' law, writing it

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* Note that v is the volume of the *whole system*.

$$\sigma = k\left(\frac{D}{M}\right)^{\frac{2}{3}} (t_c - t - \delta),$$

where δ is a small number, approximately 6. The "Eötvös constant" k, they found to be 2.1. However, later research has shown that the number k is not a constant for all liquids, and that the use of this law as a method of measuring degree of association is not reliable. Other suggestions have been made, such as one by van der Waals based on thermodynamical reasoning, viz.,

$$\sigma = \sigma_0\left(1 - \frac{t}{t_c}\right)^n.$$

In this equation n is a constant for all liquids and

$$\sigma_0 = k(p_c^2\, t_c)^{\frac{1}{3}},$$

where k is a constant for all liquids and p_c and t_c are critical pressure and temperature. Experimental research shows that this result also is not exact; although n for a number of common organic liquids does not vary by more than a few per cent from 1.21. Katayama (*Sci. Reports Tohoku Imp. Univ.* [1], **4**, 373 (1916)) has suggested a modification of Eötvös' law in the form

$$\sigma = k\left(\frac{D - d}{M}\right)^{\frac{2}{3}} (t_c - t),$$

where d is the density of the vapor; and actually an elimination of $t_c - t$ from this and the equation suggested by van der Waals, taking n to be 1.2, gives a relation

$$\sigma = C(D - d)^4$$

discovered empirically by McLeod (*Trans. Faraday Soc.*, **19**, 38, (1923)) which holds accurately for a great number of organic liquids over a wide range of temperature. In it C is a constant, different for each liquid, and the relation is of great value in comparing densities.

As stated, these relations all have an important bearing on molecular complexity in liquids, a problem which still awaits solution. In applying them it is assumed that M changes with temperature since with increasing temperature polymerized molecules tend to dissociate into the simple molecules which exist in vapor, and the assumed truth of the expressions enables relative values of M to be found at each temperature. Although too great reliance cannot be placed on the conclusions deduced, Bennett and Mitchell (*Zeit. physik. Chem.*, **84**, 475, (1913) and Bennett (*Trans. Chem. Soc.*, **107**, 351, (1915)) have shown that the "*total* molecular surface energy"

$$\left(\sigma - t\frac{\partial\sigma}{\partial t}\right)(MV)^{\frac{2}{3}}$$

is a better quantity to use for this purpose than the "free molecular surface energy"

$$\sigma(MV)^{\frac{2}{3}}$$

of Eötvös, and that this leads to more consistent conclusions concerning molecular association.

35. Heat of Adsorption

Returning to Gibbs work, the reader will find on pages 271, 272 a reference to the "amount of heat necessary to keep the phases from altering while the surface of discontinuity is extended." If $\partial\sigma/\partial t$ is negative, as appears to be the general rule, this heat is positive and if not supplied the temperature of the surface will fall, causing an increase of tension. Actually, if $\partial\sigma/\partial t$ were positive, an increase of tension would also occur since in this case the heat would be negative, so that if transfer of heat were prevented the surface would warm up. Now this heat must be carefully distinguished from "heat of adsorption," which is heat required to get rid of *adsorbed* molecules on the surface, and bears some resemblance to latent heat. We can best illustrate its nature by a reference once more to Micheli's work on adsorption of gases (*Phil. Mag.* **3**, 895 (1927)). As stated earlier, he showed, if P is the partial pressure of the vapor, that

$$\Gamma = kP,$$

and his results also show that for a given vapor over the water surface the constant k decreases markedly with rise of temperature. Thus for pentane at 25°C., k is 75×10^{-7}; at 35°C. it is 35.8×10^{-7}; for hexane the decrease is from 106×10^{-7} to 55.5×10^{-7}, and for heptane from 256×10^{-7} to 115×10^{-7}, a rise of ten degrees roughly halving the value of k in each case. This means that a rise of temperature causes desorption, the partial pressure P being kept constant. Thus desorption requires heat and adsorption is accompanied by an evolution of heat. We can, of course, use the well-known Clapeyron relation to obtain this molecular heat of adsorption. Thus from the equation

$$H_n = Rt^2 \frac{d \log P_n}{dt}$$

heats of adsorption can be calculated in the same way as latent heats are calculated, where P_n is the partial pressure of the vapor when n mols are adsorbed per unit area and H_n is the heat of adsorption at constant temperature and pressure at the same stage of adsorption. If P_{n_1} and P_{n_2} are values of P_n at the temperatures t_1 and t_2, then as a first approximation

$$H_n = \frac{R\, t_1\, t_2\, (\log P_{n1} - \log P_{n2})}{t_1 - t_2}.$$

Also, if k_1 and k_2 are the values of the constant k for t_1 and t_2, $k_1 P_{n_1} = k_2 P_{n_2}$, and therefore

$$H_n = \frac{R\, t_1\, t_2\, (\log k_2 - \log k_1)}{t_1 - t_2}.$$

Thus "the heat of adsorption is independent of the particular value of *n*, so that each equal increment in the amount adsorbed is accompanied by the same heat evolution. This is, of course, only possible when the adsorbed layer is so diffuse that the amount already adsorbed has no effect on further adsorption." Micheli calculates the heats of adsorption for pentane, hexane, and heptane, and finds them to be 13.6, 11.7, 14.6. He notes that the probable error may amount to 20 per cent and so he takes the three results to be roughly the same; at all events they do not show any sign of increasing with the number of carbon atoms in the molecule; even an accuracy of only 20 per cent precludes that possibility. From this he concludes that the molecules do not lie flat on the surface, for then we should expect the heat of adsorption to be roughly proportional to the number of carbon atoms in the molecule. (The reader will recall a similar line of argument by Langmuir in section VII of this commentary.) "These considerations, then, furnish some additional support for the conclusion that an end CH_3 group forms the only point of attachment to the water surface."

A good deal of work on heat of adsorption and "heat of wetting" has been carried out at the interfaces between solids and gases or vapors, but reference to this will be deferred until we reach the subsection of Gibbs' treatise which deals with solid-fluid interfaces.

36. Dependence of σ on the "Age" of a Surface

With reference to the subject discussed on pp. 272–274 of Gibbs' work, namely, the effect on the surface tension of creating a fresh surface, it may not be out of place to mention the suggestion sometimes made, that because ordinary liquids, even "pure," are constituted really of different molecules (since they differ in degree of polymerization or chemical activity) they should display a surface tension different at a fresh surface from that which would exist there some time after formation. This argument is clearly based on the adsorption law and the assumption that there are at least two types of molecules in the liquid, one of which produces a higher surface tension than the other. On forming a fresh surface, the composition of the surface layer would be identical with that in the interior, but with lapse of time the molecules affording the greater surface tension would tend to leave the surface and a fall in surface tension would be observed. In his book (page 152) Adam criticizes the experimental evidence which has been brought forward to substantiate the hypothesis on which this argument is built, pointing out that the purely mechanical effects of the appliances employed could easily account for the initial elevation of water in a capillary tube apart from the effect of the postulated increase of surface tension at the beginning. He states that until apparatus capable of dealing with liquid surfaces not older than 0.005 sec. has been devised, the question cannot be regarded as settled. Undoubtedly contamination produces change in surface tension.

XIII. The Influence of Gravity

37. The Variation of p, σ, μ_1, μ_2, $\cdots$ with Depth in a Liquid. An Apparent Inconsistency in Gibbs' Argument. The Argument Justified

Before proceeding to consider the question of stability of equilibrium it will be well to dispose of the subject of equilibrium in itself and to proceed at once to deal with the subject matter treated on pages 276–287 of Gibbs' treatise which is the natural continuation of the considerations raised earlier on pages 144–147. The conditions obtained there still hold, with the additional important equations [614] and [615]. There is a certain economy in the notation at the outset of this subsection. In [599], for instance, $\delta\int D\epsilon^V$ stands really for the sum of a number of terms such as

$$\delta\int D\epsilon'^V + \delta\int D\epsilon''^V + \delta\int D\epsilon'''^V + \ldots$$

each referring to one homogeneous mass, while $\delta\int gzDm^V$ is a double sum such as

$$\begin{aligned}&\delta\int gz_1'\,Dm_1'{}^V + \delta\int gz_2'\,Dm_2'{}^V \ldots\\&+\delta\int gz_1''Dm_1''{}^V + \delta\int gz_2''Dm_2''{}^V \ldots\\&+ \text{etc.}\end{aligned}$$

Also $\delta\int D\epsilon^S$ consists of as many terms as there are surfaces, and similar remarks apply to $\delta\int gzDm^S$. It will be quite sufficient to limit the system to one with two homogeneous masses and one surface of discontinuity.

The transformation from the equation [599] to [600] is one which calls for careful scrutiny on the part of the reader. The difficulties are hinted at in the beginning of the paragraph succeeding equation [600], but perhaps the fact that they are fully met in the transformation may not be so "evident" to every reader as it was to Gibbs. Take for instance one inclusive term such as $\delta\int D\epsilon^V$ in [599]. (We omit accents and consider it as referring for the moment to either homogeneous mass.) We know that

$$D\epsilon^V = tD\eta^V - pDv + \mu_1 Dm_1{}^V + \mu_2 Dm_2{}^V$$

and so $\delta\int D\epsilon^V$ should apparently be equal to

$$\delta\int tD\eta^V - \delta\int pDv + \delta\int \mu_1 Dm_1{}^V + \delta\int \mu_2 Dm_2{}^V.$$

But if we carry the sign of variation, δ, within the sign of integration, we ought in strict mathematical procedure to write $\delta\int tD\eta^V$ as $\int\delta(tD\eta^V)$, $\delta\int pDv$ as $\int\delta(pDv)$ and so on. Instead they are written $\int t\delta D\eta$, $\int p\delta Dv$, etc. Later, near the top of page 280, $\int p\delta Dv$ is transformed back into $\int\delta(pDv) - \int\delta pDv$, and to the unwary this might seem to a veritable "trick" in order to get the first two terms of equation [611] and thereafter the equation [612]. The matter seems still more mystifying when we consider an inclusive term in [599] such as $\delta\int gzDm^V$; for it is written $\int\delta(gzDm^V)$ and expanded to $\int gz\delta Dm^V + \int g\delta zDm^V$, and not merely left as equivalent to the first integral of that sum. However, the solution is not obscure when pointed out. Looking back to [15] and [497] we recall that the conditions of equilibrium without gravity are not

$$\delta(t\eta) - \delta(pv) + \delta(\mu_1 m_1) + \delta(\mu_2 m_2) = 0$$

but

$$t\delta\eta - p\delta v + \mu_1\delta m_1 + \mu_2\delta m_2 = 0.$$

When we take gravity into account p, σ, μ_1, μ_2 are no longer constant throughout a given homogeneous mass or on a given dividing surface; they are now functions of position as well as of η, v, s, m_1, m_2, and vary in value from point to point in one phase. Considering a given infinitesimal element of volume Dv in the unvaried state, it will change in size to $Dv + \delta Dv$ and will move to a new adjacent position; the value of p at its new location will vary not only for the reasons which would cause variation without influence of gravity and which have been involved in the earlier treatment of equilibrium, but also because it has moved to a different position; and the veriest tyro in hydrostatics knows that if a difference of level is produced pressure will vary. This is where great care is needed; when $p\delta Dv$ is written in [600], the δDv is multiplied by the pressure which existed *where the element Dv was situated before the variation was conceived to take place.* A similar remark applies to $\int \mu_1 \delta Dm_1^V$, $\int \sigma \delta Ds$, $\int \mu_1 \delta Dm_1^S$, etc. Now the term $\int p\delta Dv$ should be written

$$\int p'\delta Dv' + \int p''\delta Dv'', \tag{23}$$

and considering the first integral in this we can regard it as the sum of two parts, one in which the varied positions of the Dv' still remain in the volume occupied by the single accent phase before variation, and one in which the varied positions of the Dv' are to be found between the original and varied situations of the dividing surface. To evaluate the first part we shall for the moment represent the element Dv' before variation by Dv_a' and after by Dv_b', Dv_a' being situated at x, y, z and Dv_b' at $x + \delta x$, $y + \delta y$, $z + \delta z$. The value of the first part is equal to

$$\int p_a'(Dv_b' - Dv_a') = \int p_a' Dv_b' - \int p_a' Dv_a'.$$

But since the extent of integration is the same for the second of these as for the first we can write this equal to

$$\begin{aligned} \int p_a' Dv_b' - \int p_b' Dv_b' &= \int (p_a' - p_b') Dv_b' \\ = \int \{p'(x, y, z) - p'(x + \delta x, y + \delta y, z + \delta z)\} Dv' \\ = -\int \left\{ \frac{\partial p'}{\partial x}\,\delta x + \frac{\partial p'}{\partial y}\,\delta y + \frac{\partial p'}{\partial z}\,\delta z \right\} Dv'. \end{aligned}$$

Thus we have the first part of the integral $\int p'\delta Dv'$ in (23). The second part will be the integral $\int p'\delta N Ds$ throughout the region between the two positions of the dividing surface, for p' is the pressure which existed where the element $\delta N Ds$ was before it moved into the region originally occupied by the double accent phase. Hence in (23) $\int p'\delta Dv'$ is equal to the sum of a surface integral, and a volume integral, viz.,

$$\int p'\,\delta N\,Ds - \int\left(\frac{\partial p'}{\partial x}\,\delta x + \frac{\partial p'}{\partial y}\,\delta y + \frac{\partial p'}{\partial z}\,\delta z\right) Dv'.$$

In the second integral of (23) we must, in the same way, first integrate

$$-\int\left(\frac{\partial p''}{\partial x}\,\delta x + \frac{\partial p''}{\partial y}\,\delta y + \frac{\partial p''}{\partial z}\,\delta z\right) Dv''$$

throughout the original region occupied by the double accent phase and then *subtract* from this the surface integral $\int p''\delta N Ds$. Thus we find that

$$\int p'\delta Dv' + \int p''\delta Dv''$$

$$= \int (p' - p'')\,\delta N Ds - \int\left(\frac{\partial p'}{\partial x}\,\delta x + \frac{\partial p'}{\partial y}\,\delta y + \frac{\partial p'}{\partial z}\,\delta z\right) Dv'$$

$$- \int\left(\frac{\partial p''}{\partial x}\,\delta x + \frac{\partial p''}{\partial y}\,\delta y + \frac{\partial p''}{\partial z}\,\delta z\right) Dv'',$$

for which [609] is a condensed form.

With reference to the term $\int \sigma\delta Ds$, we see in just the same way that it is equal to the change produced by the variation in the integral $\int \sigma Ds$, minus the value of the integral $\int \delta\sigma Ds$, where $\delta\sigma$ is given by [608]. The term $\delta\int\sigma Ds$ consists of two parts. To see this, imagine normals drawn to the surface s at points on the boundaries between the various elements Ds. The normals projecting, as it were, from the boundary of a given Ds will form a tube which will cut out on the varied position of s a corresponding element of area whose size is $Ds[1 + (c_1 + c_2)\,\delta N]$.* All the original elements of s will thus mark out a defined

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* See the note on curvature p. 12 of this volume.

(and much the larger) part of the varied surface. This contributes to the variation of $\int \sigma Ds$ the amount $\int \sigma(c_1 + c_2)\, \delta N Ds$. But around this large portion of the varied surface there will be a narrow "rim" bounded by the varied position of the perimeter and by the line obtained by projecting the perimeter of the original surface on the varied position of the surface. Between an element Dl of the varied perimeter and the corresponding element of this projection there is a distance δT, where δT is the "component of the motion of this element which lies in the surface and is perpendicular to the perimeter." Thus this rim can be conceived as consisting of elements of area $\delta T Dl$, and we obtain in this way the second contribution to $\delta \int \sigma Ds$, viz., $\int \sigma \delta T Dl$; thus we see that

$$\int \sigma \delta Ds = \int \sigma(c_1 + c_2) \delta N Ds + \int \sigma \delta T Dl$$
$$- \int \left(\frac{\partial \sigma}{\partial \omega_1} \delta \omega_1 + \frac{\partial \sigma}{\partial \omega_2} \delta \omega_2 \right) Ds.$$

These two (condensed) terms of the original condition of equilibrium [600], viz. $-\int p \delta Dv + \int \sigma \delta Ds$, are the two which offer the most trouble in being transformed into a convenient form. When we replace them in [600] by the expressions just obtained we can rewrite the condition [600] in the form

$$\int t\, \delta D\eta^V + \int t\, \delta D\eta^S$$
$$+ \int (\mu_1' + g z_1')\, \delta D m_1'^V + \int (\mu_1'' + g z_1'')\, \delta D m_1''^V$$
$$+ \int (\mu_1^S + g z_1^S)\, \delta D m_1^S$$
$$+ \int (\mu_2' + g z_2')\, \delta D m_2'^V + \int (\mu_2'' + g z_2'')\, \delta D m_2''^V$$
$$+ \int (\mu_2^S + g z_2^S)\, \delta D m_2^S$$
$$+ \int \left\{ \left(g\gamma' + \frac{\partial p'}{\partial z'} \right) \delta z' + \frac{\partial p'}{\partial x'} \delta x' + \frac{\partial p'}{\partial y'} \delta y' \right\} Dv'$$
$$+ \int \left\{ \left(g\gamma'' + \frac{\partial p''}{\partial z''} \right) \delta z'' + \frac{\partial p''}{\partial x''} \delta x'' + \frac{\partial p''}{\partial y''} \delta y'' \right\} Dv''$$

$$+ \int \left\{ [(p'' - p') + \sigma(c_1 + c_2)]\, \delta N + g\Gamma\, \delta z^S \right.$$

$$\left. - \left[\frac{\partial \sigma}{\partial \omega_1}\, \delta\omega_1 + \frac{\partial \sigma}{\partial \omega_2}\, \delta\omega_2 \right] \right\} Ds$$

$$+ \int \sigma \delta T Dl = 0.$$

Now we introduce the usual conditions, viz.,

$$\int \delta D\eta^V + \int \delta D\eta^S = 0\,,$$

$$\int \delta D m_1{}'^V + \int \delta D m_1{}''^V + \int \delta D m_1{}^S = 0\,,$$

$$\int \delta D m_2{}'^V + \int \delta D m_2{}''^V + \int \delta D m_2{}^S = 0\,,$$

and in addition to these the further conditions that

$$\delta x',\ \delta y',\ \delta z',\ \delta x'',\ \delta y'',\ \delta z''$$

are arbitrary, and that

$$\delta z^S = \delta N \cos\theta + a_1 \delta\omega_1 + a_2 \delta\omega_2\,,$$

where $a_1 \delta\omega_1 + a_2 \delta\omega_2$ is the tangential part of the displacement of a point on the surface, a_1 and a_2 being functions of ω_1 and ω_2 and the angles between the vertical and the directions in the surface defined by $\delta\omega_1$ and $\delta\omega_2$.

It follows from the conditions of equilibrium and these additional conditions that

$$t = \text{a constant throughout the system,} \qquad [605]$$

$$\left. \begin{aligned} \mu_1{}' + g z_1{}' &= \mu_1{}'' + g z_1{}'' = \mu_1{}^S + g z_1{}^S, \\ \mu_2{}' + g z_2{}' &= \mu_2{}'' + g z_2{}'' = \mu_2{}^S + g z_2{}^S, \end{aligned} \right\} \qquad [617]$$

$$\left. \begin{aligned} \frac{\partial p'}{\partial x'} &= \frac{\partial p''}{\partial x''} = 0, \\ \frac{\partial p'}{\partial y'} &= \frac{\partial p''}{\partial y''} = 0, \\ \frac{\partial p'}{\partial z'} &= -\, g\gamma', \\ \frac{\partial p''}{\partial z''} &= -\, g\gamma'', \end{aligned} \right\} \qquad [612]$$

$$p' - p'' = \sigma(c_1 + c_2) + g\Gamma \cos\theta. \qquad [613]$$

Also

$$g\Gamma\ (a_1\,\delta\omega_1 + a_2\,\delta\omega_2) = \frac{\partial\sigma}{\partial\omega_1}\,\delta\omega_1 + \frac{\partial\sigma}{\partial\omega_2}\,\delta\omega_2.$$

This means that for any arbitrary displacement of a point in the surface in a direction tangential to the surface the variation $\delta\sigma$ in σ is equal to $g\Gamma$ multiplied by the vertical component of this displacement; for a reference to the expression for δz^S above reveals that this is the meaning of $a_1\delta\omega_1 + a_2\delta\omega_2$. Hence we have

$$\frac{\partial\sigma}{\partial z} = g\Gamma. \qquad [614]$$

To summarize the matter we see that the potential of any component does not remain constant throughout a given phase; it decreases with altitude. What remains constant throughout the phase is $\mu + gz$, and the constant value of this for a given component is the same in each homogeneous phase and on the surface of discontinuity. The pressures p' and p'' and the surface tension σ are functions of t and the constants M_1, M_2, and are therefore functions of z, and their rates of change with respect to z are given in [612] and [614]. They are independent of x and y. We have omitted the last result

$$\int \sigma\delta T D l = 0.$$

This has been written so far in too simple a form, in order to avoid causing trouble at the moment by an awkward digression. We have been considering, it will be recalled, two homogeneous phases and *one* surface of discontinuity. This would of course be realized if one phase were surrounded entirely by the other, but as in that case the dividing surface would have no perimeter at all the condition written would be meaningless. However, we are not necessarily confined to this case, but if we treat two phases in a fixed enclosure, then we must include the wall of the enclosure as a "surface of discontinuity" as well as the dividing film between the two phases. It is true that we assume that no physical or chemical changes take place in the wall, and no energy changes so caused are therefore involved, but the perimeter of the dividing surface may move along the wall (the creeping of the meniscus in a capillary tube up or down is a familiar example) and the condition above must then be written

$$\int (\sigma_1 \delta T_1 + \sigma_2 \delta T_2 + \sigma_3 \delta T_3) Dl = 0 ,$$

where δT_1 is the tangential motion (normal to Dl) in the dividing surface, δT_2 the tangential motion in the surface between the single accent phase and the wall, δT_3 that in the surface between the double accent phase and the wall, and σ_1, σ_2, σ_3 are respectively the three free surface energies between the two phases, and between each phase and the wall. This means that at any point of the perimeter

$$\sigma_1 \delta T_1 + \sigma_2 \delta T_2 + \sigma_3 \delta T_3 = 0 ,$$

and this is the well-known condition

$$\sigma_1 \cos \alpha + \sigma_2 - \sigma_3 = 0 ,$$

where α is the contact angle between the dividing surface and the wall. Actually, in the general case of several homogeneous phases and dividing surfaces, the condition is interpreted in a similar way for a number of surfaces of discontinuity (at least three) meeting in one line, as is shown at the bottom of page 281 of Gibbs' treatise.

The constants M_1, M_2 are the potentials at the level from which z is measured (positive if vertically upwards). It follows that p', p'', σ, Γ are functions of t, M_1, M_2, z. If determined by experiment these functions enable us to turn [613] into a differential equation for the surface of tension as shown in pages 282–283. Equation [620] is an approximate form of this differential equation. We refer the reader to the short note on curvature (this volume, p. 14) for an explanation of the left-hand side of it.

XIV. The Stability of Surfaces of Discontinuity

38. *Conditions for the Stability of a Dynamical System*

When the stability of a dynamical system is being investigated, the potential energy of the system is expressed as a function of the coordinates of the system. If the system were at rest in any configuration this function of the coordinates for this configuration would give the whole energy of the system. If this configuration is one of equilibrium then the partial differential coefficients of the function with respect to different coordinates are severally zero; for if $f(x_1, x_2, x_3, \ldots)$ represents the function, $x_1, x_2, x_3, \ldots$ being the coordinates, we know that to the first order of magnitude $f(x_1, x_2, x_3, \ldots)$ must not vary in value when $x_1, x_2, x_3, \ldots$ receive small arbitrary increments $\delta x_1, \delta x_2, \delta x_3, \ldots$ Thus

$$\frac{\partial f}{\partial x_1}\delta x_1 + \frac{\partial f}{\partial x_2}\delta x_2 + \frac{\partial f}{\partial x_3}\delta x_3 + \ldots = 0,$$

and since $\delta x_1, \delta x_2, \delta x_3, \ldots$ are arbitrary, it follows that

$$\frac{\partial f}{\partial x_1} = 0, \qquad \frac{\partial f}{\partial x_2} = 0, \qquad \frac{\partial f}{\partial x_3} = 0, \qquad \text{etc.}$$

We can express this simply by the condition

$$\delta f(x_1, x_2, x_3, \ldots) = 0.$$

Now the equilibrium may be stable, unstable or neutral. If we wish to investigate the matter in more detail we must consider the value of $\Delta f(x_1, x_2, x_3, \ldots)$. This is equal to the value of $f(x_1 + \delta x_1, x_2 + \delta x_2, x_3 + \delta x_3, \ldots) - f(x_1, x_2, x_3, \ldots)$ when higher powers of $\delta x_1, \delta x_2, \delta x_3$, etc. than the first are retained in the expansion of $f(x_1 + \delta x_1, x_2 + \delta x_2, x_3 + \delta x_3, \ldots)$. In many cases it is sufficient to retain the second powers and neglect those that are higher. For convenience we write $\xi_1, \xi_2, \xi_3, \ldots$ for $\delta x_1, \delta x_2, \delta x_3, \ldots$ Then by Taylor's theorem

$$\Delta f(x_1, x_2, x_3, \ldots) = \frac{\partial f}{\partial x_1}\,\xi_1 + \frac{\partial f}{\partial x_2}\,\xi_2 + \frac{\partial f}{\partial x_3}\,\xi_3 + \ldots$$
$$+ \tfrac{1}{2}\left\{\frac{\partial^2 f}{\partial x_1^2}\,\xi_1^2 + \frac{\partial^2 f}{\partial x_2^2}\,\xi_2^2 + \frac{\partial^2 f}{\partial x_3^2}\,\xi_3^2 + \ldots\right.$$
$$+ 2\,\frac{\partial^2 f}{\partial x_1\,\partial x_2}\,\xi_1\,\xi_2 + 2\,\frac{\partial^2 f}{\partial x_1\,\partial x_3}\,\xi_1\,\xi_3 + \ldots$$
$$\left. + 2\,\frac{\partial^2 f}{\partial x_2\,\partial x_3}\,\xi_2\,\xi_3 + \ldots\right\}.$$

The values of $\partial f/\partial x_1$, $\partial f/\partial x_2$, etc. are zero when $x_1, x_2, x_3, \ldots$ are the values of the coordinates for the configuration in question. For convenience let us represent the values of $\partial^2 f/\partial x_1^2$, $\partial^2 f/\partial x_2^2$, $\ldots$ $\partial^2 f/\partial x_1 \partial x_2$, $\ldots$ for the same coordinates by the symbols $a_{11}, a_{22}, \ldots a_{12}, \ldots$ The symbol a_{21} would represent $\partial^2 f/\partial x_2 \partial x_1$, but by the law of commutation for partial differentials this is the same as a_{12}. Now if the configuration is one of *stable* equilibrium, the value of $f(x_1, x_2, x_3, \ldots)$ is less at the equilibrium configuration than for any neighboring configuration. Hence if the equilibrium is stable the quadratic expression

$$a_{11}\xi_1^2 + a_{22}\xi_2^2 + a_{33}\xi_3^2 \ldots + 2a_{12}\xi_1\xi_2 + 2a_{13}\xi_1\xi_3 \ldots$$
$$+ 2a_{23}\xi_2\xi_3 + \ldots$$

is positive for any arbitrary values of $\xi_1, \xi_2, \xi_3, \ldots$ In short it is a "positive definite form."* The conditions which must be satisfied by the coefficients $a_{11}, a_{22}, \ldots a_{12}, \ldots$ for this to be the case are well-known and can be most readily expressed in terms of the determinant

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & \ldots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \ldots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \ldots & a_{3n} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & a_{n3} & \ldots & a_{nn} \end{vmatrix}$$

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* See the note on *The Method of Variations*, this volume, p. 5.

and its minor determinants. Thus if the form is to be definitely positive, this determinant, the first minors obtained by erasing any row and a corresponding column, the second minors obtained by erasing any two rows and the corresponding columns, the third minors obtained in a similar way, and so on until we reach the individual constituents of the leading diagonal, must all be positive quantities. If this is not so the form will have negative values for some sets of values of ξ_1, ξ_2, ξ_3, . . . and so the system will for some displacements not tend to return to, but will move further away from, the original equilibrium configuration. Indeed if the first minors, third minors, fifth minors and so on had one sign; the determinant, the second minors, the fourth minors and so on, the other; the system would be unstable for any displacement whatever.

39. Restricted Character of such Conditions as Applied to a Thermodynamical System

In the investigation of the stability of a thermodynamic system a similar procedure can be followed, but it suffers from one limitation which Gibbs discusses. The energy of the system is regarded as a function of the thermodynamical variables, which in the present instance specify the condition of the homogeneous masses and of the film separating them. For equilibrium $\delta\epsilon$ must be zero for any arbitrary infinitesimal variations of these variables—at least, arbitrary apart from the familiar conditions such as [481].* For stable equilibrium $\Delta\epsilon$ will be positive for all possible variations of the variables within the assigned limitations. If we then proceed to apply the method just outlined we must conceive ϵ to be formulated as a function of the variables, (the entropy, masses of components, volume, area of film) and the first and higher differential coefficients also so expressed and the tests applied. (See the proof for the thermodynamic system as given on pages 105–115, especially [173] *et seq.*) But this assumes that in any state, other than the initial one, whose energy content needs to be considered, we are regarding the energy as expressible in the same functional form of the altered values of the variables, and this implies that such other states are states of equilibrium. In consequence, this method limits us to the consideration of the stability of the initial state with reference to the neighboring *equilibrium* states, but not with regard to all neighboring states, among which may be non-equilibrium states. In the purely dynamical problem, all states of the system, equilibrium or not, have their potential energy expressible in terms of the coördinates; but in the thermodynamical problem all the states of the system cannot have their energy expressed in terms of the variables. Indeed certain values of the variables inconsistent with equilibrium may "fail to determine with precision any state of the system." The question of instability would of course offer no difficulty in this case. If near the equilibrium state in question there exist one or more other equilibrium states which under the usual conditions possess less energy, the original state is certainly unstable; that requires no consideration of non-equilibrium states. However, although there may exist neighboring states of equilibrium which might prove, on investigation by the method outlined, to be states of greater energy, we cannot be so definite about the original state being one of stable equilibrium; for the method does not preclude the possibility of the existence of non-equilibrium states of smaller energy. Having drawn the reader's attention to this matter, which we shall take up later, we proceed to a commentary on the subsection.

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* This restriction in arbitrariness would render the analytical procedure in such a case somewhat more complicated than that indicated above, but would not invalidate the general idea.

40. Stability of a Plane Portion of a Dividing Surface Which Does Not Move

At the outset Gibbs deals with the problem of stability with the limitation that the dividing surface film is plane and uniform and *is not supposed to move.* He directs attention to the possibility of a small change taking place in the variables which specify a small portion of the film, and which are a small group of the entire collection of variables specifying the whole system. Denote the small part of the film by Ds; its variables are the temperature t, its entropy $D\eta^{s\prime}$, and the masses of the components in it $Dm_a{}^{s\prime}$, $Dm_b{}^{s\prime}$, ... $Dm_g{}^{s\prime}$, $Dm_h{}^{s\prime}$, ... The change does not in the first instance involve an alteration in t, nor in the position or size of Ds; but $Dm_a{}^{s\prime}$ is changed to $Dm_a{}^{s\prime\prime}$, etc., and $D\eta^{s\prime}$ to $D\eta^{s\prime\prime}$; in short, the single accent indicates the initial state, the double accent the state after change. Of course the changes of mass in this small portion of the film must be drawn from (or passed into) the remaining portion of the system, i.e., the rest of the film and the homogeneous masses. Similarly as the total entropy must remain constant the rest of the system must experience a change of entropy equal to $D\eta^{s\prime} - D\eta^{s\prime\prime}$. The homogeneous masses are assumed to be relatively so great that these small changes in them do not practically affect the values of the potentials μ_a, μ_b, ... of the components a, b, ... which are both in the volume phases and the surface phase, so that no accenting is required in writing them. A similar remark applies to the large remaining portion of the film. However, as regards the g, h, ... components which only occur at the surface, the value of the potentials will alter in Ds from $\mu_g{}'$, $\mu_h{}'$, ... to $\mu_g{}''$, $\mu_h{}''$, ..., but for the rest of the film they will remain at their original values $\mu_g{}'$, $\mu_h{}'$, ... for the reason already specified, viz., that the changes of masses and entropy in this part of the film are relatively too insignificant to effect a change in the potentials. It is very important to keep in mind the fact that it is assumed that there are components in the surface which are not in the homogeneous masses; otherwise the discussion of this particular special case would be pointless. The new condition of the portion Ds of the film is supposed to be one which is still consistent with equilibrium between it and the neighboring homogeneous masses. (This of course places the limitation mentioned above on the generality of the investigation. It will be quite definite in its answer concerning instability, but leaves a possibility of failure to lead to a definite conclusion concerning stability.) In consequence, the energy of the small portion, Ds, of the film will be $D\epsilon^{s\prime\prime}$, where $D\epsilon^{s\prime\prime}$ is the same function of the variables t, $D\eta^{s\prime\prime}$, $Dm_a{}^{s\prime\prime}$, etc., and Ds, that $D\epsilon^{s\prime}$ is of t, $D\eta^{s\prime}$, $Dm_a{}^{s\prime}$, etc., and Ds. The energy of Ds is therefore increased by $D\epsilon^{s\prime\prime} - D\epsilon^{s\prime}$. The energy of the rest of the system is increased by an amount which is equal to

$$t\delta\eta' + \mu_a'\delta m_a' + \mu_b'\delta m_b' \ldots + \mu_g'\delta m_g' + \mu_h'\delta m_h' + \ldots$$

where $\delta\eta'$, $\delta m_a'$, etc., are the increases of entropy and of the masses of the various components in the rest of the system. But we have seen that these increases are $D\eta^{s'} - D\eta^{s''}$, $Dm_a^{s'} - Dm_a^{s''}$, etc. Hence the increase in the energy of the rest of the system is

$$t(D\eta^{s'} - D\eta^{s''}) + \mu_a'(Dm_a^{s'} - Dm_a^{s''}) \ldots + \mu_g'(Dm_g^{s'} - Dm_g^{s''}) + \ldots \tag{24}$$

The increase in energy of the whole system is therefore

$$D\epsilon^{s''} - D\epsilon^{s'} + t(D\eta^{s'} - D\eta^{s''}) + \mu_a(Dm_a^{s'} - Dm_a^{s''}) \ldots + \mu_g'(Dm_g^{s'} - Dm_g^{s''}) + \ldots$$

where we have dropped as unnecessary the accents over μ_a, μ_b, ..., the potentials which do not alter between the first and second state. Now by [502] applied to the small portion of the film, which it will be remembered is in an equilibrium condition in both states

$$D\epsilon^{s'} = t\,D\eta^{s'} + \sigma'\,Ds + \mu_a Dm_a^{s'} \ \ldots + \mu_g'\,Dm_g^{s'} + \ldots,$$

$$D\epsilon^{s''} = t\,D\eta^{s''} + \sigma''Ds + \mu_a Dm_a^{s''} \ \ldots + \mu_g''Dm_g^{s''} + \ldots,$$

where σ' and σ'' are the values of the surface tension in the small portion in the two states. Hence we easily see that the increase in energy of the whole system is equal to

$$(\sigma'' - \sigma')Ds + (\mu_g'' - \mu_g')Dm_g^{s''} + (\mu_h'' - \mu_h')Dm_h^{s''} + \ldots \tag{25}$$

This is the expression which occurs just a little below the middle of page 241, stated for a small portion of the film Ds. If this is a positive quantity for all changes, infinitesimal or finite, the system is stable. To discuss instability we must consider two different cases. The expression (25) may be negative even when $Dm_a^{s'}$, ... $Dm_g^{s'}$, ... differ by infinitesimal amounts from $Dm_a^{s''}$, ... $Dm_g^{s''}$, ... and therefore μ_g', μ_h', ... σ' differ by infinitesimal amounts from μ_g'', μ_h'', ... σ''. If this be so, the system is definitely unstable in the first state. However, it may be possible that the expression (25) is positive for infinitesimally small values of $\sigma'' - \sigma'$, $\mu_g'' - \mu_g'$, $\mu_h'' - \mu_h'$, etc., but would be negative for finite values of these changes. The system would satisfy the theoretical conditions of stability which, as any student of dynamics knows, only compare the state of a system with other states infinitesimally near it. Yet the system, as Gibbs points out, would not be stable in the practical sense; for a disturbance which, while being small, would be sufficient to carry the system beyond the infinitesimally near states of larger energy would bring it to states of less energy from which it would not tend to return to the first state. Perhaps it may not be out of place to remind the reader that the quantities $Dm_a{}^{s'}$, $Dm_a{}^{s''}$, etc., are not variations of mass; they are the small masses initially and finally present in the small part of the film. Further, that $Dm_a{}^{s''} - Dm_a{}^{s'}$, etc., are not necessarily small *compared to* $Dm_a{}^{s'}$, $Dm_a{}^{s''}$, etc. They are small compared to the masses in the rest of the film and the homogeneous masses; that is why we can use them correctly in the expression (24). But since they are *finite* changes in respect to the small portion Ds of the system, they produce finite changes in the surface tension and the $g, h, \ldots$ potentials there, so that we can regard $\sigma'' - \sigma'$, $\mu_g'' - \mu_g'$, $\mu_h'' - \mu_h'$, etc., as finite differences if necessary. This small digression on the meaning of the D symbol may serve to illuminate the point about practical instability.

The argument can now be extended to the whole film. Having effected the change in one small part of the film, we can carry it out for another small part, changing entropy and masses there so as to produce the $g, h, \ldots$ potentials and surface tension, μ_g'', μ_h'', $\ldots$ σ'', which exist in the first small part, and so on. This is simply the procedure indicated by the integrations on Gibbs, I, 240. The changed condition in the film is therefore uniform in nature throughout and is one which could exist in equilibrium with the homogeneous masses in their practically unchanged condition. The difference of energy *in the whole system* for the two states of the film is

$$(\sigma'' - \sigma')s + m_g{}^{s''}(\mu_g'' - \mu_g') + m_h{}^{s''}(\mu_h'' - \mu_h') + \ldots \qquad (26)$$

41. Three Conclusions Drawn from the Analysis in Subsection (40)

This disposes of the analytical steps on these pages of Gibbs' treatise. There are three conclusions based on them. The first appears at the top of page 240. As presented it is somewhat elusive, but we can put it as follows. It is possible that the potentials μ_g'', μ_h'', ... which correspond to the masses $m_a{}^{s''}$, $m_b{}^{s''}$, ... $m_g{}^{s''}$, $m_h{}^{s''}$, ... may be respectively equal to the potentials μ_g', μ_h', ... which correspond to $m_a{}^{s'}$, $m_b{}^{s'}$, ... $m_g{}^{s'}$, $m_h{}^{s'}$, ... (Of course, the potentials μ_a, μ_b, ... remain unchanged in any case.) If this is so, then by (26) $(\sigma'' - \sigma')s$ must be positive if the single accent state is to be a stable state of equilibrium; i.e., $\sigma'' > \sigma'$. There appears to be a contradiction here; we have seen that σ is a function of t and the potentials $\mu_a{}^S$, $\mu_b{}^S$, ... $\mu_g{}^S$, $\mu_h{}^S$, ... and it appears absurd to assume that σ'' is different from σ' at all if μ_a, μ_b, ... μ_g', μ_h', ... do not differ in value from μ_a, μ_b, ... μ_g'', μ_h'', ... But this is to overlook the possibility of σ being a double-valued or multi-valued function of the temperature and potentials, so that if the variables μ_a, μ_b, ... μ_g, μ_h, ... experience a change of values corresponding to changes in the masses of the components, and presently retake the same values, the surface tension may not retake its original value. (We have already made use of this result in an earlier part of this commentary to show that if there are, say, a "gaseous" and a "liquid" phase in the surface of discontinuity, they must, if stable, have the same value of σ.)

The second conclusion drawn concerns the sign of σ. In the argument so far there has been no displacement or deformation of Ds. It is implied also that s is practically plane. If Ds being plane is deformed, its area must increase. This will necessitate the withdrawal of small amounts of the components from the homogeneous masses or from the rest of the film in order to maintain the nature of the film in Ds unchanged. These amounts, as before, will be infinitesimal for the rest of the system. The amounts will have gone from a place where the potentials have been at certain values to a place where they are at the same values. This will cause no change in the energy of the system; the term of the energy expression which will have altered will be σDs which will become $\sigma(Ds + \delta Ds)$.

The energy change will be $\sigma \delta Ds$. For stability this must be positive, and as δDs is positive, σ must be positive. The paragraphs on pages 240, 241 elaborate this.

The third conclusion occurs in the paragraph beginning towards the bottom of Gibbs, I, 241. It is very elusive indeed and the final sentences of the paragraph are not very happily chosen for a reader not expert in mathematical technique. First of all the reader must realize that there may be a whole continuous series of states of the system differing in the nature of the film, which will be states of stable equilibrium. A change from any one of them to any state infinitesimally near it, whether a non-equilibrium state or one of its equilibrium neighbors, will involve an increase of energy. Let the single and double accents refer to two neighboring infinitesimally different states of stable equilibrium. We have seen then that

$$(\sigma'' - \sigma')s + (\mu_g'' - \mu_g')m_g^{S''} + (\mu_h'' - \mu_h')m_h^{S''} + \ldots$$

must be positive. But exactly the same reasoning will show that

$$(\sigma' - \sigma'')s + (\mu_g' - \mu_g'')m_g^{S'} + (\mu_h' - \mu_h'')m_h^{S'} + \ldots$$

must also be positive. Now write μ_g for $\mu_g^{S'}$, μ_h for $\mu_h^{S'}$, ... $\mu_g + \Delta\mu_g$ for $\mu_g^{S''}$, $\mu_h + \Delta\mu_h$ for $\mu_h^{S''}$, etc.; σ for σ', $\sigma + \Delta\sigma$ for σ'', m_g^S for $m_g^{S'}$, m_h^S for $m_h^{S'}$, ... $m_g + \Delta m_g$ for $m_g^{S''}$, $m_h + \Delta m_h$ for $m_h^{S''}$, etc. From the expression given four lines above we obtain the result

$$s(-\Delta\sigma) + m_g^S(-\Delta m_g) + m_h^S(-\Delta m_h) + \ldots > 0,$$

which is just the equation preceding [521]. Considering [521] we may write it, remembering that μ_g, μ_h, ... are the only quantities which are varying,

$$\begin{aligned}&\frac{\partial\sigma}{\partial\mu_g}\Delta\mu_g + \frac{\partial\sigma}{\partial\mu_h}\Delta\mu_h + \ldots \\ &\quad + \frac{1}{2}\left\{\frac{\partial^2\sigma}{\partial\mu_g^2}(\Delta\mu_g)^2 + \frac{\partial^2\sigma}{\partial\mu_h^2}(\Delta\mu_h)^2 \ldots + 2\frac{\partial^2\sigma}{\partial\mu_g\,\partial\mu_h}\Delta\mu_g\Delta\mu_h + \ldots.\right\} \\ &+ \text{higher powers} < -\Gamma_g\Delta\mu_g - \Gamma_h\Delta\mu_h - \ldots\end{aligned}$$

Now by [508]

$$\frac{\partial \sigma}{\partial \mu_g} = -\Gamma_g, \qquad \frac{\partial \sigma}{\partial \mu_h} = -\Gamma_h, \ldots$$

Hence, if we neglect the cubes and higher powers, we can write

$$\frac{\partial^2 \sigma}{\partial \mu_g^2}(\Delta\mu_g)^2 + \frac{\partial^2 \sigma}{\partial \mu_h^2}(\Delta\mu_h)^2 \ \ldots \ + 2\frac{\partial^2 \sigma}{\partial \mu_g \partial \mu_h}\Delta\mu_g\Delta\mu_h + \ldots < 0.$$

Now at the outset of this section of the commentary, on page 606, we dealt with the conditions which render such a quadratic expression always positive or always negative in value. We see that in order to comply with the present condition of negativity a series of determinants beginning with

$$\frac{\partial^2 \sigma}{\partial \mu_g^2}, \quad \begin{vmatrix} \dfrac{\partial^2 \sigma}{\partial \mu_g^2} & \dfrac{\partial^2 \sigma}{\partial \mu_g \partial \mu_h} \\ \dfrac{\partial^2 \sigma}{\partial \mu_h \partial \mu_g} & \dfrac{\partial^2 \sigma}{\partial \mu_h^2} \end{vmatrix}, \text{ and so on,}$$

will be alternately negative and positive for the values of the variables μ_g, μ_h, ... which exist in the "single-accent" film, i.e., $\mu_g{}^{S'}$, $\mu_h{}^{S'}$ ... Looking at the question from a purely mathematical point of view, if, in addition to these conditions,

$$\frac{\partial \sigma}{\partial \mu_g}, \ \frac{\partial \sigma}{\partial \mu_h}, \ \ldots$$

were all zero for the same values of μ_g, μ_h, ... then σ regarded as a function of μ_g, μ_h, ... would have a maximum value for these same values of μ_g, μ_h, ... This is the meaning of the cryptic remark at the end of the paragraph (p. 242). But of course the "necessary conditions relative to the first differential coefficients" are *not* fulfilled; in other words $\partial\sigma/\partial\mu_g$ is not zero for the values $\mu_g{}^{S'}$, $\mu_h{}^{S'}$, ... of μ_g, μ_h, ...; it is equal to $-\Gamma_g{}'$, and so on. To be sure, the conditions for the second differential coefficients are satisfied, but for a reader who is not familiar with the concrete forms of these conditions, the way in which the conclusion is stated in Gibbs' text is somewhat confusing. We have limited the matter to the second differential coefficients, as that is sufficient to make the meaning of the sentence more apparent to the reader. (As the order of $\mu_g, \mu_h, \mu_i, \ldots$ is immaterial, the conditions are, that the constituents in the principal diagonal of the determinant

$$\begin{vmatrix} \dfrac{\partial^2\sigma}{\partial\mu_g^2} & \dfrac{\partial^2\sigma}{\partial\mu_g\partial\mu_h} & \dfrac{\partial^2\sigma}{\partial\mu_g\partial\mu_i} & \ldots \\ \dfrac{\partial^2\sigma}{\partial\mu_h\partial\mu_g} & \dfrac{\partial^2\sigma}{\partial\mu_h^2} & \dfrac{\partial^2\sigma}{\partial\mu_h\partial\mu_i} & \ldots \\ \dfrac{\partial^2\sigma}{\partial\mu_i\partial\mu_g} & \dfrac{\partial^2\sigma}{\partial\mu_i\partial\mu_h} & \dfrac{\partial^2\sigma}{\partial\mu_i^2} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix}$$

and all the minors of the third, fifth, seventh, etc. order, formed by erasing the necessary number of rows and corresponding columns, shall be negative, while the minors of the second, fourth, etc. order formed by similar erasures shall be positive in value.)

42. Determination of a Condition Which Is Sufficient though Not Necessary for Stability when the Dividing Surface Is Not Plane and Is Free to Move

The investigation so far has been limited by the proviso that the surface is plane and does not move. The removal of this limitation renders the problem more difficult, although it is easy to derive a condition which in this case will insure stability, without actually being necessary for it. Gibbs' treatment of this occurs at the very end of this subsection, on pages 251, 252, but it is so relatively simple compared to the other material of the subsection that the reader may find it helpful to have his attention directed to it at once. To make the presentation as direct as possible, consider a system with two homogeneous masses separated by one surface of discontinuity, the whole enclosed in a rigid envelop. We can suppose that two fine tubes inserted through the envelop put each mass in communication with a very large external mass which contains all the component substances at suitable temperature and potentials; this is also enclosed in an external rigid envelop and bounded internally by the envelop enclosing the system. A movement of the surface of discontinuity in the system entails in general a change in the volumes of the homogeneous masses of the system. This does not involve any change in the potentials of the various components in them or in the surface (in so far as they are components in the surface); for the amounts of components withdrawn from or passed into these masses are passed into or withdrawn from the external mass, and that is so large that the amounts are relatively too small to affect the potentials in it. For the two masses we have equations such as these:

$$\begin{aligned}\Delta\epsilon' &= t\,\Delta\eta' - p'\,\Delta v' + \mu_1\Delta m_1' + \ldots,\\ \Delta\epsilon'' &= t\,\Delta\eta'' - p''\Delta v'' + \mu_1\Delta m_1'' + \ldots,\end{aligned}$$

and an equation

$$\Delta\epsilon''' = t\,\Delta\eta''' + \mu_1\Delta m_1''' + \ldots$$

for the external mass, since its volume does not change. For the surface

$$\Delta\epsilon^S = t\,\Delta\eta^S + \sigma\Delta s + \mu_1\Delta m_1{}^S + \ldots$$

The variations may be finite* since t, μ_1, μ_2, ... remain constant; p' and p'' are not necessarily equal since we are not assuming the surface to be plane, but since each of them is a definite function of t, μ_1, μ_2, ..., each remains constant. Now if

$$\Delta\epsilon' + \Delta\epsilon'' + \Delta\epsilon''' + \Delta\epsilon^S > 0$$

the complete system is stable as regards the movement of the surface. Since the total entropy and masses are constant we can state that if

$$\sigma\Delta s - p'\Delta v' - p''\Delta v'' > 0$$

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* Finite, that is, with reference to the system; they are small compared to the external mass.

the complete system is stable. Now if the complete system is stable, the original system (without communication with external mass) is certainly stable. For blocking up the tubes and isolating the original system is equivalent to imposing a mechanical constraint on the complete system; and it is well known in mechanics that if a dynamical system is in a stable state of equilibrium, the imposition of a constraint does not upset that condition. Indeed this fact is intuitively obvious. The inequality [549] is simply the same result extended to a wider system. But, of course, the condition may not be *necessary* for stability of equilibrium as regards movement of the surfaces; in short it insures stability for the system under wider conditions than are actually envisaged at the outset and so under more restricted conditions than these the system might be stable without [549] being satisfied.

43. Gibbs' General Argument Concerning Stability in Which the Difficulty Referred to in Subsection (39) Is Surmounted

The general argument of Gibbs on the conditions of stability or instability will be found on pages 246–249. (On pages 242–246 he discusses the problem by a more specialized method which can be passed by for the moment.) At the outset of the argument he raises the point which we have already noted, that if we use an analytical method, analogous to that employed in dynamics, we are virtually excluding from consideration those states of the system which are not in equilibrium and for which the fundamental equations are not valid and the usual functional forms for energy, etc. have no meaning, since in these states the systems cannot be specified with precision by values of the usual variables. That is dealt with on page 247. He proposes then to surmount this obstacle by introducing the consideration of an "imaginary system" which is fully described at the top of page 248. This system agrees with the actual system in all particulars in the initial state, which is one of equilibrium for both systems, though whether it is stable or not for the actual system is the point under consideration. His argument, however, may be framed so as to exclude any express consideration of his imaginary system and may appear simpler on that account. We may, for simplicity of statement, consider a system of two homogeneous masses with one dividing surface; the statement can easily be extended to cover wider cases. Let us suppose the system is varied to a state in which the conditions in the phases and dividing surface are not conditions of equilibrium as regards temperature and potentials, and the dividing surface is changed in position; also let it be found that this is a state of smaller energy than the unvaried state, the total entropy and total masses however being the same as originally. Now imagine that the dividing surface is "frozen," as it were, in the varied position. (This is equivalent to the postulate of Gibbs as to constraining the surface by certain fixed lines.) If left alone, the system in this "frozen varied" state would tend to a new state of equilibrium; we are conceiving that its total energy is not altered from the varied value, nor, of course, the individual volumes of each phase; the total masses are not to vary either, but there may still be passage of components through and into or out of the dividing surface (its rigid condition is not to interfere with that). In this third state (second varied state) the entropy will of course have increased above that of the first varied state and so above that of the original state of equilibrium. Now by the withdrawal of heat (the rigidity of the system being still preserved) we can arrive at a third varied state, *which is also one of equilibrium,* in which the total entropy, etc., will be as originally, but the energy less than that of the second varied state and therefore less than that of the original state. Of course, on imagining the surface now to be "thawed out," that is, the constraint on it removed, we cannot be sure that the varied pressures established in the phases and the varied tension in the surface will be consistent with the curvature of the dividing surface, which must of course remain in the same varied position all the time (for if it moves from this the volumes and therefore the potentials will change from the values arrived at in the last state and might not be in equilibrium in the two phases in the final state). The point, however, is that if there is a non-equilibrium state infinitesimally near the original state which is one of less energy, there is also a quasi-equilibrium state infinitesimally near which is also one of less energy—using the word "quasi-equilibrium" to designate a state in which the equilibrium conditions for the temperature and potentials are satisfied, but not the mechanical condition which connects the difference of pressures in the two phases with the tension and curvature. More than that, if there is no quasi-equilibrium varied state which has less energy than the unvaried state there is no non-equilibrium varied state which has less energy; for as we have just seen if there were one such non-equilibrium state there must be at least one such quasi-equilibrium state. Thus if there is no equilibrium state, or quasi-equilibrium state, infinitesimally near to the given state which has a less energy than that state, it is one of stable equilibrium. Now all such states, equilibrium or quasi-equilibrium, are states for which ϵ is given by the fundamental expression in terms of the variables η', η'', η^S, v', v'', s, m_1', m_2', ..., and so we can apply the analytical method of maxima and mimima outlined above to the solution of the problem of the stability of a given state, without concerning ourselves about the mechanical equilibrium of the dividing surface in any adjacent state.

44. Illustration of Gibbs' Method by a Special Problem

The problem with which Gibbs illustrates this method on pages 249, 250 concerns the system which we have used, for simplicity, to expound the method, with the limitation that the edge of the surface of discontinuity is constrained not to move, so that the two fluid phases are, as it were, separated by an orifice to the edge of which the film adheres. The whole is enclosed in a rigid, non-conducting envelop. Suppose a small variation takes place from this condition of equilibrium, so that the volumes change from v' and v'' to $v' + \delta v'$ and $v'' + \delta v''$ where, of course, $\delta v' + \delta v'' = 0$. This will entail a change in the position and size of the surface, its area becoming $s + \delta s$. The total quantity of any component remains unchanged, but the potentials in the masses and at the surface change. Since the first component has a given amount for the whole system

$$\gamma_1'v' + \gamma_1''v'' + \Gamma_1 s = \text{constant},$$

and therefore

$$(\gamma_1' - \gamma_1'')\,\delta v' + \Gamma_1 \delta s + \left(v' \frac{\partial \gamma_1'}{\partial \mu_1} + v'' \frac{\partial \gamma_1''}{\partial \mu_1} + s \frac{\partial \Gamma_1}{\partial \mu_1}\right) \delta \mu_1$$
$$+ \left(v' \frac{\partial \gamma_1'}{\partial \mu_2} + v'' \frac{\partial \gamma_1''}{\partial \mu_2} + s \frac{\partial \Gamma_1}{\partial \mu_2}\right) \delta \mu_2 + \text{etc.} = 0.$$

(This is the equation [546] on page 251, generalized to deal with the variation of several potentials and not merely of one.) There are several points about this equation which require careful consideration before we proceed, for they reveal the nature of the assumptions implied. First, it is clearly assumed that in the varied state the potentials of any component are still equal in the two masses, and also equal to the varied potential of that component at the surface; for example, the first component has the potential $\mu_1 + \delta\mu_1$ everywhere. Thus we are assuming that the varied state is one which does "not violate the conditions of equilibrium relating to temperature and potentials." Second, since the equation is meaningless unless $\partial\gamma_1'/\partial\mu_1$, $\partial\gamma_1''/\partial\mu_1$, $\partial\Gamma_1/\partial\mu_1 \ldots$ have definite values, we are assuming that $\gamma_1' = \partial v'/\partial\mu_1$, $\gamma_1'' = \partial v''/\partial\mu_1$, $\Gamma_1 = -\partial\sigma/\partial\mu_1$ and so on, and that $\partial\gamma_1'/\partial\mu_1$, etc., are obtained from these by further differentiations. So it is implied that the fundamental equations are valid. The equation is not quite in the form of [546]; to make it so we should have to write the first three terms in the form

$$\left(\gamma_1' - \gamma_1'' + \Gamma_1 \frac{ds}{dv'}\right)\delta v'.$$

But this implies that s is a function of v'; otherwise ds/dv' has no meaning. This, however, is taken care of by the necessary condition of stable equilibrium that the surface of tension has the minimum area for given values of the volumes v' and v'' separated by it. This minimum-area condition is not sufficient for stable equilibrium, but it is necessary, and therefore in discussing the stability of a state of equilibrium there would be no necessity to proceed further if we knew that it was not satisfied. This condition therefore gives a unique value to s for a given value of v' (or v''; $v' + v''$ is constant). So s is a single-valued function of v', and ds/dv' has a definite meaning. We can obtain $n - 1$ similar equations

$$\left(\gamma_2' - \gamma_2'' + \Gamma_2 \frac{ds}{dv'}\right) \delta v' + \left(v' \frac{\partial \gamma_2'}{\partial \mu_1} + v'' \frac{\partial \gamma_2''}{\partial \mu_1} + s \frac{\partial \Gamma_2}{\partial \mu_1}\right) \delta \mu_1 + \text{etc.} = 0,$$

etc.

These n equations give us the theoretical means to calculate the n quantities $d\mu_1/dv'$, $d\mu_2/dv'$, . . . in terms of the state of the system. In this way we see, as is stated at the top of page 250, that all the quantities relating to the system may be regarded as functions of v'. Thus we can obtain dp'/dv'; for it is equal to

$$\frac{\partial p'}{\partial \mu_1} \frac{d\mu_1}{dv'} + \frac{\partial p'}{\partial \mu_2} \frac{d\mu_2}{dv'} + \ldots = \gamma_1' \frac{d\mu_1}{dv'} + \gamma_2' \frac{d\mu_2}{dv'}.$$

Similarly

$$\frac{dp''}{dv'} = \gamma_1'' \frac{d\mu_1}{dv'} + \gamma_2'' \frac{d\mu_2}{dv'} + \ldots$$

and

$$\frac{d\sigma}{dv'} = -\Gamma_1 \frac{d\mu_1}{dv'} - \Gamma_2 \frac{d\mu_2}{dv'} - \ldots$$

In the initial state we assume that $p' - p'' = \sigma(c_1 + c_2)$; in the varied state the pressures and surface tension $p' + \delta p'$, $p'' + \delta p''$, $\sigma + \delta\sigma$ are of course the same functions of t, $\mu_1 + \delta\mu_1$, . . . as p', p'', σ are of t, μ_1, . . . But nowhere do we have to assume that

$$(p' + \delta p') - (p'' + \delta p'') = (\sigma + \delta\sigma)(c_1 + \delta c_1 + c_2 + \delta c_2),$$

so that the varied state *need not be a state of equilibrium as regards the condition expressed by equation [500]*.

The energy of the system, depending as it does on the variables of the system, can, as we have just seen, be expressed as a function of v'. The energy in the varied state is by Taylor's theorem

$$\epsilon + \frac{d\epsilon}{dv'}\,\delta v' + \frac{1}{2}\,\frac{d^2\epsilon}{dv'^2}\,(\delta v')^2 + \ldots$$

For equilibrium $d\epsilon/dv'$ must be zero. For stable equilibrium we must have the additional condition

$$\frac{d^2\epsilon}{dv'^2} > 0.$$

The amplification of this condition on page 250 to the form [544] is easy; in [544] we regard dp'/dv', dp''/dv', $d\sigma/dv'$ as given by the equations above, and of course ds/dv', d^2s/dv'^2 can be calculated from the geometrical form of the system and the fixed perimeter of the film. Equation [547] is the result for the special case when one potential only is variable.

45. An Approach to this Problem from a Consideration of the Purely Mechanical Stability of the Surface

Thus we have learned the general theoretical method of dealing with stability when sufficient knowledge is available concerning the functional forms of the various energy functions. It involves no trouble concerning the mechanical stability of the surface of discontinuity, which in a manner of speaking takes care of itself. However, it is interesting to approach the problem from that angle as well, and this is what Gibbs does in the pages immediately preceding those on which we have just commented. Going back we take up this aspect at the bottom of page 244 where a system just like the one we have been considering is posited. (We are not assuming a circular orifice.) Passing by the two short paragraphs at the top of page 245 (which are unimportant for our present purpose) we have the relation for equilibrium

$$p' - p'' = \sigma(c_1 + c_2),$$

where, as before, p', p'', σ are functions of v' the volume of one phase. A slight variation of the surface of discontinuity will cause a change in $p' - p''$, σ and $c_1 + c_2$. If there is to be stability the surface must tend to return to its original position and $(p' + \delta p') - (p'' + \delta p'')$ must be less than $(\sigma + \delta\sigma)\,(c_1 + \delta c_1 + c_2 + \delta c_2)$, so that

$$\delta(p' - p'') < (c_1 + c_2)\delta\sigma + \sigma\ \delta(c_1 + c_2).$$

As every one of the variables can be represented as a function of v' it follows that, for mechanical stability of the surface,

$$\sigma\,\frac{d(c_1 + c_2)}{dv'} > \frac{dp'}{dv'} - \frac{dp''}{dv'} - (c_1 + c_2)\,\frac{d\sigma}{dv'}.$$

Now it can be shown that

$$c_1 + c_2 = \frac{ds}{dv'},$$

where s is the area of the surface, bounded as it is by the edge of the orifice. (See the note on curvature, p. 10 of this volume.) Hence it follows that

$$\sigma\,\frac{d^2s}{dv'^2} > \frac{dp'}{dv'} - \frac{dp''}{dv'} - \frac{d\sigma}{dv'}\cdot\frac{ds}{dv'},$$

which is just equation [544]. The problem can be completed as on page 251. Thus we see that the same conclusion is reached as before when we took no special heed of mechanical stability and merged that stability, as it were, in the general method of dealing with stability with reference to the neighboring equilibrium and quasi-equilibrium states. This provides still further justification for the validity of the general method. The only point of special importance about the problem on page 245 concerns the assumed circularity of the orifice. One then has special values for ds/dv' and d^2s/dv'^2. These can be derived from the special geometry of the case as outlined in the middle of page 245; by the aid of the equations there one can prove that

$$\frac{dr}{dv'} = -\frac{r - x}{\pi r x^2}, \qquad \frac{ds}{dv'} = \frac{2}{r},$$

and

$$\frac{d^2s}{dv'^2} = -\frac{2}{r^2}\,\frac{dr}{dv'} = \frac{2(r - x)}{\pi r^3 x^2},$$

and so equation [547] takes on the special form [540] in this case.

The reader will now find no difficulty in following the matter on pages 242–244. The special corollary concerning the system in which "the interior mass and surface of discontinuity are formed entirely of substances which are components of the external mass" (of which a drop of water in an indefinitely large mass of vapor is a good illustration) offers a good example for applying the *sufficient* test which is given on page 252, and on which we have already commented. Thus, the interior volume being v' and the radius r, let the radius increase to $r + \delta r$. Now it is a feature of the method, which must not be overlooked, that Δs and $\Delta v'$ are not to be taken as $8\pi r \delta r$ and $4\pi r^2 \delta r$ respectively; that overlooks the higher powers of δr which are vital for the purpose of the test. Actually, if we merely retain first powers of δr, $\delta s = 8\pi r \delta r$, $\delta v' = 4\pi r^2 \delta r$ and $\delta v'' = -4\pi r^2 \delta r$; therefore

$$\Sigma(\sigma \delta s) - \Sigma(p \delta v) = \{\sigma.8\pi r - (p' - p'')4\pi r^2\}\,\delta r,$$

which is zero (as it should be for equilibrium). But

$$\Delta s = 8\pi r \delta r + 4\pi(\delta r)^2,$$

and

$$\Delta v' = 4\pi r^2 \delta r + 4\pi r(\delta r)^2 + \frac{4\pi}{3}(\delta r)^3 = -\Delta v''.$$

Hence

$$\Sigma(\sigma\,\Delta s) - \Sigma(p\,\Delta v)$$

$$= 4\pi\sigma(\delta r)^2 - 4\pi r(p' - p'')\,(\delta r)^2 - \frac{4\pi}{3}(p' - p'')\,(\delta r)^3$$

$$= 4\pi\sigma\left\{(\delta r)^2 - 2(\delta r)^2 - \frac{2(\delta r)^3}{3r}\right\}$$

$$= -\,4\pi\sigma(\delta r)^2$$

(provided δr is small compared to r). This is negative for any sign of δr. Hence the sufficient test of stability is not satisfied.

Of course this test is not conclusive on the matter; it gives strong presumptive evidence that the system is not stable, but as it is not absolutely necessary for stability the matter has to be clinched by the necessary test which is actually applied in the text. This goes beyond the purely mechanical considerations, and uses the fact that p', p'' and σ do not change if there is a large enough external mass to draw on to maintain constancy of composition in the phases. Hence if $p' - p'' = 2\sigma/r$ then $p' - p'' > 2\sigma/r'$ if $r' > r$, and so the internal sphere expands encroaching on the outer phase; whereas $p' - p'' < 2\sigma/r'$ if $r' < r$ and the internal sphere gradually disappears as the outer phase encroaches on it.

The treatment of stability on pages 285–287 will now be easily followed. Certain obvious generalizations to be introduced when gravity is taken into account are given there, the result in [625] being, for instance, a wider statement of the result [549] on page 252.

XV. The Formation of a Different Phase within a Homogeneous Fluid or between Two Homogeneous Fluids

46. A Study of the Conditions in a Surface of Discontinuity Somewhat Qualifies an Earlier Conclusion of Gibbs Concerning the Stable Coexistence of Different Phases

The possibility of the stable coexistence of different phases has been treated earlier in Gibbs' treatise without reference to the special nature of the surfaces of discontinuity separating them. (See pages 100–115 of Gibbs.) There it is shown that if the pressure of a fluid is greater than that of any other phase of its independently variable components which has the same temperature and potentials, the fluid is stable with respect to the formation of any other phase of these components; but if the pressure is not as great as that of some such phase, it will be practically unstable. "The study of surfaces of discontinuity throws considerable light upon the subject of the stability of such homogeneous fluid masses as have a less pressure than others formed of the same components . . . and having the same temperature and the same potentials. . . ." Suppose for instance we have two phases of the same components whose pressures are the functions $p'(t, \mu_1, \mu_2, \ldots)$ and $p''(t, \mu_1, \mu_2, \ldots)$ of temperature and potentials (written $p'(t, \mu)$ and $p''(t, \mu)$ for brevity). A surface of discontinuity between two such phases would have a surface tension which is the function $\sigma(t, \mu_1, \mu_2 \ldots)$, or $\sigma(t, \mu)$, of the same temperature and potentials. For the purposes of the argument we are assuming that these functional forms are known. Now if the surface were plane, the condition would not be one of equilibrium; the phase for which the pressure function has the larger value at given values of $t, \mu_1, \mu_2, \ldots$ would grow at the expense of the other. Actually, if the phase of greater pressure, say the single-accent phase, were confined in a sphere whose radius is equal to

$$\frac{2\,\sigma(t, \mu)}{p'(t, \mu) - p''(t, \mu)}$$

there would be equilibrium when surrounded by the phase of smaller pressure. However, as we know, if the second mass is indefinitely extended the equilibrium is unstable (provided there are no components in the internal phase which are not in the external), and the first mass if just a little larger will tend to increase indefinitely; while one a little smaller would tend to decrease, leaving the field to the second mass. So under certain circumstances the mass of smaller pressure, if indefinitely extended around the mass of larger pressure would be the one to grow, thus somewhat qualifying the conclusion from the earlier part of Gibbs' discussion. However, since the possibility of this qualification depends on the smallness of the internal mass of the higher pressure phase, it becomes necessary to take into account the case where this mass "may be so small that no part of it will be homogeneous, and that even at its center the matter cannot be regarded as having any phase of matter in *mass*." Pages 253–257 of Gibbs treat this problem. The reader is to keep in mind that the phase which might be conceived to grow out of this non-homogeneous nucleus under favorable circumstances is supposed to be known, with its fundamental equations, as well as, of course, the second phase inside which it may grow; i.e., $p'(t, \mu)$, $p''(t, \mu)$ and $\sigma(t, \mu)$ are to be regarded as known functions. Let E represent the energy of the system if the space were entirely filled with the second phase; then $E + [\epsilon]$, by the definition of $[\epsilon]$ in the text, is the energy of the system with the non-homogeneous nucleus formed inside. But of course $[\epsilon]$ is not the ϵ^S (nor are $[\eta]$, $[m_1]$, ... the same as η^S, $m_1{}^S$, ...) by means of which σ is defined. As usual, we postulate a definite position for the dividing surface, a sphere of radius r. For the purpose of defining ϵ^S this is supposed to be filled with the homogeneous phase of the first kind right up to the dividing surface, the second phase occupying the space beyond; the energy then would be

$$E + v' (\epsilon_V' - \epsilon_V''),$$

where $v' = \frac{4}{3}\pi r^3$, and so

$$\begin{aligned} \epsilon^S &= E + [\epsilon] - \{E + v'(\epsilon_V' - \epsilon_V'')\} \\ &= [\epsilon] - v'(\epsilon_V' - \epsilon_V''), \end{aligned}$$

with similar definitions for η^S, $m_1{}^S$, ... as in the text.

47. *The Possibility of the Growth of a Homogeneous Mass of One Phase from a Heterogeneous Globule Formed in the Midst of a Homogeneous Mass of Another Phase*

Imagine the heterogeneous globule to be formed in the midst of the originally homogeneous mass of the second phase, the formation being achieved by a reversible process and the globule being in equilibrium. The additional entropy and masses, $[\eta]$, $[m_1]$, $[m_2]$, ... in the space where the globule is situated are supposed to be drawn from the rest of the system, which may be conceived to be so large that these withdrawals do not appreciably affect the temperature and potentials in the exterior parts. The change of energy in the exterior will be a *decrease* of amount

$$t[\eta] + \mu_1[m_1] + \mu_2[m_2] + \dots$$

The increase of energy in the space occupied by the globule is $[\epsilon]$. Hence the increment of energy in the whole system, above that of a system in which the second phase occupies the whole space, is

$$[\epsilon] - t[\eta] - \mu_1[m_1] - \mu_2[m_2] - \ldots,$$

which is denoted by W (Equation [552]). This is a function of the temperature and potentials and is independent of any selected situation for the dividing surface; so we write it $W(t, \mu)$. Now, as Gibbs himself notes at the outset of this subsection, the method of selecting the surface of tension in former cases is hardly applicable here, and it is not at all clear just how he proposes to select it since his remarks concerning the $C_1\delta c_1 + C_2\delta c_2$ terms do not appear very convincing. As he says, the $\frac{1}{2}(C_1 - C_2)\ \delta(c_1 - c_2)$ term does not concern us for spherical surfaces. But what of the $\frac{1}{2}(C_1 + C_2)\ \delta(c_1 + c_2)$ term? However, on closer investigation it becomes clear what he does. In the earlier parts he showed that the special choice which got rid of the $C_1\delta c_1 + C_2\delta c_2$ terms placed the dividing surface so that it satisfied the condition

$$p' - p'' = \sigma(c_1 + c_2),$$

so here he takes the dividing spherical surface to have a radius given by

$$r = \frac{2\ \sigma(t, \mu)}{p'(t, \mu) - p''(t, \mu)}.$$

This is tantamount to assuming that the ideal system which replaces the heterogenous globule and exterior mass, supposed to be in equilibrium, is a homogeneous sphere of the first phase, an ideal surface with the tension $\sigma(t, \mu)$ and the exterior mass of the second phase, which is in equilibrium mechanically, as well as with regard to temperature and potentials. The radius of this surface then becomes a definite function of the temperature and potentials; for as is shown on page 254

$$\begin{aligned}\sigma s &= \epsilon^S - t\eta^S - \mu_1 m_1{}^S - \mu_2 m_2{}^S - \ldots \\ &= W + v'(p' - p''),\end{aligned}$$

and since

$$r(p' - p'') = 2\sigma,$$

and

$$s = 4\pi r^2, \qquad v' = \frac{4\pi r^3}{3},$$

it follows easily that

$$W(t, \mu) = \tfrac{1}{3}\, s\sigma(t, \mu) = \tfrac{1}{2} v' \{p'(t, \mu) - p''(t, \mu)\},$$

and so

$$\left.\begin{aligned} r &= \left[\frac{3\, W(t, \mu)}{2\pi\, \{p'(t, \mu) - p''(t, \mu)\}}\right]^{\frac{1}{3}} \\ &= \left[\frac{3\, W(t, \mu)}{4\pi\sigma(t, \mu)}\right]^{\frac{1}{2}} \end{aligned}\right\}. \qquad [556]$$

The reader can now follow the course of the reasoning on pages 256–257. If, for given values of temperature and potentials, there are two phases possible with different pressures such that equilibrium is possible with an inner *homogeneous* sphere of the higher pressure phase, an exterior phase of lower pressure and a surface of discontinuity, we see that since r in [556] is then a real positive quantity and $p' - p''$ is positive, $W(t, \mu)$ is positive for these values of $t, \mu_1, \mu_2, \ldots$ In other words, this system has actually greater energy than the system made up of the lower pressure phase alone, and so there would be no tendency for the latter system to transform naturally into the first. If however, by any external agency, the spherical mass of this size and constitution were formed, then it would be unstable, as we have seen, at least if the external mass is indefinitely extended, which means in practice that if any disturbance caused a small increase in the size of the sphere, it would tend to increase still further up to a limit set by the extent of the exterior phase. Now if, by alteration of the temperature and potentials of the system, we find values $t_0, \mu_{10}, \mu_{20}, \ldots$ for which

$$p'(t_0, \mu_0) = p''(t_0, \mu_0),$$

then $W(t_0, \mu_0)$ is infinite for these values. It is to be noted that near the top of page 255 Gibbs says that W *can only become* infinite when $p' = p''$, which is true enough in view of [555] or [556]; for since at such values of the potentials equilibrium between the two phases could only occur at a plane surface, r must be infinite, and so W *might be* infinite, but not necessarily infinite on account of [556], since by that equation r could be infinite when $p' = p''$ even if W were finite. But in any case W could not be infinite under other conditions. However, on page 256, Gibbs says quite definitely that when $p' = p''$ the value of W *is* infinite, thus invoking implicitly some other reason than the purely mathematical, but not perfectly cogent, argument just cited. Apparently it is the physical fact that an infinitely extended sphere of the first phase will have an excess of energy of infinite amount over the same sphere of the second phase, since $v'(\epsilon_V' - \epsilon_V'')$ tends to infinity with v' if $\epsilon_V' - \epsilon_V''$ remains positive and finite, which must be assumed to be true or otherwise the discussion would be pointless. Returning therefore to the state indicated by the values t_0, μ_{10}, μ_{20}, . . . let the temperature and potentials change gradually from these so as to make $p'(t, \mu)$ increasingly greater than $p''(t, \mu)$; $W(t, \mu)$ will gradually decrease. It may ultimately reach the value zero, but if it does so then r and σ will also vanish for the values of t, μ_1, μ_2, . . . which make W vanish, the difference $p' - p''$ still being finite. For any values of temperature and potentials in the range up to this stage the conditions of stability remain as stated; the second phase is stable, there would be no tendency for a "fault" to form in it. At this stage the matter is in doubt. The argument in the last few lines of page 256 is very subtle indeed. The quantity r may be zero, but this does not imply that a heterogeneous globule might not exist in equilibrium since r is not the radius of the globule. If, however, the globule dimension vanishes when r is zero, Gibbs says that the second phase would be unstable at the corresponding value of temperature and potentials. To see this we must remember that if, at any values of temperature and potentials, we created by any physical means the internal mass corresponding to the finite r for these values of t, μ_1, μ_2, . . ., then the slightest disturbance causing a slight growth in its size would cause the first phase to encroach on the second; but, of course, finite energy would be required for the initial creation of the sphere before the infinitesimal disturbance in the right direction is applied. But if conditions were such that "zero globule" corresponded exactly to "zero r," no finite energy would be required to create the globule; any infinitesimal impulse in the right direction producing any globule however small would produce one larger than the "critical globule," which in this case is "zero globule," and at once the encroachment of the first phase on the second phase would begin. This argument does not apply if the globule does not vanish when r reaches zero, and the second phase is not unstable in the strict sense. Gibbs clearly regards the second case as the most general in nature. Doubtless he had in mind the example of the formation of water drops in saturated vapor. This instance is a good illustration of the application of the abstract reasoning of these pages. When a drop of water is in equilibrium with its vapor in a large enclosure, the vapor, over its convex surface, is supersaturated as compared with vapor over a plane surface; there is a tendency, on the slightest disturbance in the right direction, for the drop to grow in size (as we have frequently pointed out); as it does so its surface flattens and the equilibrium vapor around it decreases in pressure and density, as it naturally would do if it were being in part condensed. Nevertheless, it is a commonplace physical fact that it is next to impossible to *start* condensation in a mass of saturated vapor quite free from dust particles or ions.

48. The Possibility of the Formation of a Homogeneous Mass between Two Homogeneous Masses

We now pass on to the possibility of the formation of a fluid mass between two other fluid masses. The latter are denoted by the letters A and B. In the discussion on pages 258–261 they are supposed to be capable of being in equilibrium with one another when meeting *at a plane surface*, so that the functions $p_A(t, \mu)$ and $p_B(t, \mu)$ are to be equal to each other for all values of $t, \mu_1, \mu_2, \ldots$ On page 262 the problem is generalized, but in the meantime this condition is to be kept well in mind.

Now a third fluid mass C is conceived to exist, made up entirely of components which belong to A or B; i.e. C, having no components other than those in A and B, might conceivably form at the surface dividing A and B, and we are once more supposed to know the fundamental equations of this fluid C so that $p_C(t, \mu)$ is a known function whose numerical value can therefore be calculated for given values of t, μ_1, $\mu_2, \ldots$ In addition, $\sigma_{AB}(t, \mu)$, $\sigma_{AC}(t, \mu)$, $\sigma_{BC}(t, \mu)$ are also known functions. For the problem to be not merely trivial it is essential that $\sigma_{AB}(t, \mu)$ should not be greater than $\sigma_{AC}(t, \mu) + \sigma_{BC}(t, \mu)$. To see this conceive a very thin layer of C to be situated between A and B. This is equivalent to a dividing surface between A and B whose surface tension is $\sigma_{AC} + \sigma_{BC}$. Referring to the previous subsection on conditions of stability (Gibbs, I, 240), we see that if $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$ this is a more stable state than if A and B exist with the ordinary surface of discontinuity between them having the surface tension σ_{AB}, which is presumably greater than $\sigma_{AC} + \sigma_{BC}$. Thus for such a condition the problem is settled offhand—the layer of C would certainly form on the slightest disturbance. The problem is really worth considering if $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, or if $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$. Although in the latter case a plane film of C would obviously be unstable for a reason similar to that just given, a lentiform film might develop and so a quite definite problem is posited in this case also. In a paper on emulsification (*J. Phys. Chem.*, **31,** 1682, (1927)) Bancroft criticizes the statement that σ_{AB} cannot be larger than $\sigma_{AC} + \sigma_{BC}$, but seems to be under a misapprehension as to the situation. Gibbs on page 258 does not assert that as a general rule for three such fluids σ_{AB} cannot be greater than $\sigma_{AC} + \sigma_{BC}$; he merely, for the purposes of the problem he is discussing, rules out of account fluids for which such an inequality would be true, presumably (as the writer has pointed out definitely) on the grounds that the problem does not exist; it is solved in the very statement of such a condition.

Now if the temperature and potentials have such values that $p_C < p_A(t, \mu)$ (and of course $< p_B(t, \mu)$), the phase cannot form under any circumstances; for if it formed as a plane sheet between A and B (or as an anticlastic sheet for which $c_1 + c_2$

is zero) p_C would have to be equal to p_A or p_B, and if in the form of a lentiform mass p_C would have to be greater than p_A or p_B. Hence A and B in contact would be quite stable as regards the formation of C in such a range of values of t, $\mu_1, \mu_2, \ldots$ If we now consider the range of values of these quantities for which $p_C(t, \mu) \gtreqqless p_A(t, \mu)$, we have to deal with the two cases which arise; (1) when $\sigma_{AB}(t, \mu) = \sigma_{AC}(t, \mu) + \sigma_{BC}(t, \mu)$; (2) when $\sigma_{AB}(t, \mu) < \sigma_{AC}(t, \mu) + \sigma_{BC}(t, \mu)$.

(1) If $p_C(t, \mu) = p_A(t, \mu)$ there would just be equilibrium with a plane sheet of C between A and B, since the surface tensions between A and C, and B and C would just balance the surface tension between A and B in the portion where A and B meet. On the other hand if we varied t, μ_1, μ_2, ... to values t', μ_1', μ_2', ... such that $p_C(t', \mu') > p_A(t', \mu')$, ($p_B(t', \mu')$ still remaining equal to $p_A(t', \mu')$ as postulated originally), then equilibrium could not be maintained unless the surfaces separating A and B from C became concave towards the latter phase, tending towards a lens form. This would upset the balance of the surface tensions at the edge where the surface A–B meets the surfaces A–C and B–C. The conditions of this equilibrium can, for purely mathematical purposes, be regarded as equivalent to the equilibrium of three forces. Now the directions of the forces equivalent to σ_{AC} and σ_{BC} are no longer opposite to that equivalent to σ_{AB}. The force equivalent to σ_{AB} is greater than the resultant of the inclined forces equivalent to σ_{AC} and σ_{BC} since $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$.* Hence the edge tends to move outward, i.e., the mass C tends to increase and in so doing draws on the masses A and B for material, and so alters the phases in such a way as to bring them to such values that the equality of p_C to p_A will be restored. We see that in this case there is a tendency for the mass C to form between A and B.

(2) If $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$ the argument of the previous paragraph breaks down. Clearly, no plane sheet of C can form between A and B when $p_C = p_A$, the force equivalent to σ_{AB} being too small to pull it out, as it were, against the force equiv-

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* As is well-known, this is a convenient way of dealing with the fact that if an outward displacement of the edge were made there would be a diminution of free surface energy.

alent to $\sigma_{AC} + \sigma_{BC}$. If, however, the temperature and potentials are such that $p_C > p_A$, then presumably a lentiform mass might be in equilibrium both as regards pressures and also surface tensions, since the resultant of the force equivalent to σ_{AC} and σ_{BC} being less than their numerical sum could possibly be equal and opposite to the force equivalent to σ_{AB}. However, the argument on pages 259, 260 of the original shows that the existence of such a lentiform mass would yield a system of greater energy than the one from which it starts. Hence in general there would be no tendency to form it. The mathematical steps of the argument will offer no trouble provided the reader notes one or two points. Let us designate by X' the center of the surface $EH'F$, and by X'' that of the surface $EH''F$. The cosine of the angles between EI and the tangent to $EH'F$ at E is $(r' - x')/r'$. The area of the spherical cap, represented by $EH'F$ in Gibbs' Figure 10 and denoted by s_{AC}, is known to be $2\pi(1 - \cos\theta')r'^2$, where θ' is the angle $EX'H'$; so that, since $\cos\theta' = (r' - x')/r'$, the area is $2\pi r'x'$. The volume of the spherical sector standing on s_{AC} with its centre at X' is $\frac{1}{3}s_{AC}\cdot r' = \frac{2}{3}\pi r'^2 x'$. The volume of the cone standing on the base s_{AB} (i.e., the circle with EF as diameter) is $\frac{1}{3}\, s_{AB}\cdot X'I = \frac{1}{3}\pi R^2(r' - x')$. Hence the volume of the spherical segment between s_{AB} and s_{AC}, being equal to the difference of the sector and cone, is as given in [566].

So far we have maintained the condition $p_A(t, \mu) = p_B(t, \mu)$. If, however, this condition be abandoned, and if the functions are such that in general $p_A(t, \mu) > p_B(t, \mu)$, all the preceding line of reasoning can easily be adapted to the wider condition. This is done on pages 262–264. As before, the condition $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$ is set aside. If $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, a thin film of C would just be in equilibrium between the surfaces of A and B, which would have a curvature given by $c_1 + c_2 = (p_A - p_B)/\sigma_{AB}$ provided that

$$p_C(t, \mu) = \frac{\sigma_{BC}(t, \mu)\, p_A(t, \mu) + \sigma_{AC}(t, \mu)\, p_B(t, \mu)}{\sigma_{BC}(t, \mu) + \sigma_{AC}(t, \mu)}, \qquad [571]$$

as proved on page 262. If $p_C(t, \mu)$ were less than this critical value the film would not form. If the values of $t, \mu_1, \mu_2, \ldots$

were in the range for which $p_C(t, \mu)$ is greater than the right-hand side of the above equation, the film would form, tending to get into the lens shape at first and then, as its growth drew on the adjacent masses A and B for material and modified the potentials so as to restore the condition given by equation [571], would spread out in the film again. If, as in (2) of previous paragraphs, the phases are in such a condition of temperature and potentials that $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$, we can show that a mass

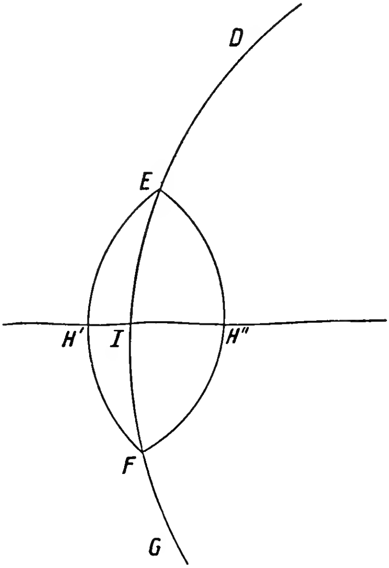

FIG. 5

of C will not tend to form on the surface between A and B, curved as before to the radius given above, even when $p_C(t, \mu)$ is greater than the critical value on the right hand of [571]. This requires a repetition of the proof on pages 260, 261 with the surface $DEIFG$ in Figure 10 of Gibbs regarded as curved and not plane; the adaptation of it to this wider geometrical condition is given on page 263 (see Fig. 5). The area represented by $EH'F$ is s_{AC}, by $EH''F$ s_{BC}, by EIF s_{AB}. V_A is the volume represented by $EIFH'$, V_B by $EIFH''$, and V_C is the sum of these.

The geometry of the figure is not so simple now, and we cannot make a direct calculation of W as on page 261. The device which Gibbs uses is stated with such conciseness in the sentences toward the bottom of page 263 that the implications involved in them had better be more fully expounded. If the state indicated did form in a natural way, it would happen in some such fashion as this. Beginning at an initial stage of temperature and potentials t_0, μ_{10}, μ_{20}, . . . for which

$$p_C(t_0,\ \mu_0) = \frac{\sigma_{BC}(t_0,\ \mu_0)\ p_A(t_0,\ \mu_0) + \sigma_{AC}(t_0,\ \mu_0)\ p_B(t_0,\ \mu_0)}{\sigma_{BC}(t_0,\ \mu_0) + \sigma_{AC}(t_0,\ \mu_0)},$$

we would gradually alter the temperature and potentials in such a way as to make $p_C(t,\ \mu)$ grow larger than the value of the corresponding expression on the right-hand side when $(t,\ \mu)$ is substituted for $(t_0,\ \mu_0)$. Notice that this would probably involve a gradual change in the curvature of that portion of the surface not embraced by the lens of C, as $p_A(t,\ \mu) - p_B(t,\ \mu)$ and $\sigma_{AB}(t,\ \mu)$ would probably change in value as t, μ_1, μ_2, . . . change in value. The process would end up in the condition and size indicated in the figure. Now to judge if this would happen *naturally* we need not consider so complicated a change. We have only to conceive any reversible process in which the system begins as imagined with the lens of C formed, and ends up in a final state in which A and B are separated by a surface having the same curvature, but with no lens there. That is, in the final state the temperature and potentials would be the same as they are at the end of the process which is supposed to have formed the lens originally. This is the process conceived by Gibbs, and what we have to do is to determine the sign of the energy change in this conceived process. During it the pressure in A and in B, as well as the surface tension between A and B, will remain at one set of values; i.e., p_A, p_B, σ_{AB} will be constant during the process. We are also to conceive that between A and C and between B and C are membranes which gradually contract, keeping at constant tensions which are equal to the values of σ_{AC} and σ_{BC} in the initial state of this process, i.e., when the lens of C exists in its fully formed state. These membranes are not to be permeable. The necessary amount of the fluids A and B can be fed in from large reservoirs through narrow tubes let in through the exterior envelop of the whole system, and the liquid C can be passed out through a similar tube into a reservoir of C in which the potentials and pressure can be adjusted; for throughout this process the one variable is the pressure of the fluid C in the gradually contracting lens. It is very necessary to observe that for equilibrium at each stage of the process this pressure *increases* with contraction of the lens, as can be readily seen by considering the simple case of a spherical membrane contracting with a constant external pressure on it and a constant tension in it. This conceptual process may help the reader to realize that the sentence near the bottom of page 263, beginning: "It is not necessary that this should be physically possible . . . ," is not an entirely arbitrary statement supporting a doubtful line of reasoning. Now let x stand for this internal pressure which increases from a value p_C' which exists in the fully formed lens and ends up at a larger value p_C'' when the lens just disappears. During the process the values of the surface areas between A and C, and between B and C will change, and we will represent them as functions of x, viz. $s_1(x)$ and $s_2(x)$, respectively; the initial values of these functions are S_{AC}, S_{BC} and the final values zero. The value of the part of the surface which would lie between A and B extended into the lens, and which decreases as the lens contracts, we will represent by $s_3(x)$; its initial value is S_{AB} and final value is zero. Similarly $v_1(x)$ and $v_2(x)$ will respectively represent the volumes between the surface A–C and the surface A–B extended into the lens, and between the surface B–C and the surface A–B so extended, while $v_3(x)$ will represent their sum, the volume of the whole lens at the stage when the internal pressure is x. The initial values of $v_1(x)$, $v_2(x)$ and $v_3(x)$ are V_A, V_B and V_C respectively; their final values are zero. Now consider the function of x, $f(x)$, defined by

$$f(x) = \sigma_{AC}\, s_1(x) + \sigma_{BC}\, s_2(x) - \sigma_{AB}\, s_3(x)$$

$$+ p_A\, v_1(x) + p_B\, v_2(x) - x v_3(x).$$

The initial value of this function is the quantity W defined in equation [573]. Its final value is zero. If we differentiate it with respect to x we find that

$$\begin{aligned} df(x) = [&\sigma_{AC}\, ds_1(x) + \sigma_{BC}\, ds_2(x) - \sigma_{AB}\, ds_3(x) \\ &+ p_A\, dv_1(x) + p_B\, dv_2(x) - x\, dv_3(x)] \\ &- v_3(x)dx, \end{aligned}$$

and by the fact that there is equilibrium at every stage of this process, which is conceived to take place reversibly, the expression inside the square brackets on the right-hand side is zero. Hence

$$df(x) = -v_3(x)dx.$$

Integrating we obtain

$$f(p_C'') - f(p_C') = -\int_{p_C'}^{p_C''} v_3(x)\, dx.$$

Since the upper limit p_C'' is *larger* than p_C', as we have mentioned above, and since $v_3(x)$ is a positive quantity throughout, the integral on the right-hand side must be positive also. Therefore the expression on the right-hand side is negative. Hence

$$f(p_C') > f(p_C'').$$

But $f(p_C'')$ is zero, since at the final stage $s_1(x)$, $s_2(x)$, . . . and $v_3(x)$ are all zero. Hence $f(p_C')$, or W, is positive. Now W is the energy excess in the initial state of the system over the final state. Since it is positive, the initial state of the system has really more energy than the final state, and moreover it is free energy, as the expression [573] shows. Thus the initial state would be unstable and so would not tend to form.

The treatment of stability given by Gibbs in this subsection and the one preceding must form an important part of any body of principle from which one may hope to obtain in time a satisfying explanation of the colloidal state. Looking back to page 241 of Gibbs, the reader will see that he comes to the conclusion that "the system consisting of two homogeneous masses and the surface of discontinuity with the negative tension is . . . at least practically unstable, if the surface of discontinuity is very large, so that it can afford the requisite material without sensible alteration of the values of the potentials." In consequence Gibbs excludes from the discussion of stability surfaces with negative tensions. Nevertheless the proviso about the size of the surface is important; for if it is not satisfied the conclusion may not be entirely valid, and so stability might be insured in cases where the interfacial surface is very small. Another instance where the conclusion might not be justified would arise if one of the masses took the form of a stratum so thin that it no longer had the properties of a similar body in a less laminated shape. (See the remark at the bottom of Gibbs I, page 240.)

The reader's attention is drawn to these points because in the treatment of the colloid state negative interfacial tensions must come into consideration. A large drop within another medium will only break up "spontaneously" into two or more drops if the free energy of the latter system is less than that of the single drop. As the sum of the surfaces of the separate drops is certainly greater than the surface of the parent drop, this is impossible with a positive interfacial tension; but a decreased free energy becomes a possible result if the tension is negative. In a paper published in the *Z. physik. Chem.*, **46**, 197 (1903) Donnan showed that from the point of view of the Laplace-Gauss theory of capillary forces (briefly outlined in the introductory sections of this article) it was possible to introduce negative interfacial tensions and draw the conclusion that "in certain cases the theory leads us to predict the spontaneous production of extremely fine-grained heterogeneous mixtures, in which one phase is distributed throughout another in a state of very fine division." Of course the difficulty of the problem is not in simply applying the notion of a negative tension, but in demonstrating that at a certain critical thickness the free energy of a film which is thinning out reaches a minimum and thereafter increases if further thinning is continued, or that at a definite size a drop reaches a similar critical state as regards its free energy.

Considerations of space prevent us from anything more than a passing reference to this very important theoretical problem; but the interested reader will find further discussions, which bring in thermodynamical principles and the effects of surface electric charges, in papers by R. C. Tolman (*J. Am. Chem. Soc.*, **35**, 307, 317 (1913)) and N. von Raschevsky (*Z. f. Physik*, **46**, 568 (1928); **48**, 513 (1928); **51**, 571 (1928)). In particular, Raschevsky's papers emphasize the fact that in addition to the purely surface phenomena a further important factor consists in the rate at which differences of concentration arising from a fast enough velocity of diffusion may give rise to inhomogeneities in the drop.

XVI. The Formation of New Phases at Lines and Points of Discontinuity

49. The Possible Growth of a Fifth Surface at a Line of Discontinuity Common to Four Surfaces of Discontinuity Separating Four Homogeneous Masses

Pages 287–300 deal with fresh possibilities in the way of new formations in addition to the natural processes studied in pages 252–264. It might be possible under certain circumstances for a new *surface* phase to develop in a system consisting of more than three homogeneous masses. If there were three homogeneous masses a surface of discontinuity would already exist between any pair, but if four masses were in existence and four surfaces of discontinuity had one line in common, there would be no surface between two pairs of the masses, and the problem arises as to the possibility of the growth of a fifth surface between such a pair. This problem is treated in pages 287–289.

The condition of equilibrium used is stated in equation [615]. In Figure 11 on page 287 of Gibbs, the common line is supposed to run perpendicular to the plane of the paper. We consider σ_1, σ_2, σ_3, σ_4 to be the four tensions in the surfaces *A–B*, *B–C*, *C–D*, *D–A* of which the lines in the figure are supposed to be sections by the plane of the paper. Conceive *any* virtual displacement of the line of discontinuity to an adjacent position which is cut by the plane of the paper in a point O'. (Not as represented in Figure 12, however, but with four displaced lines all branching from O'.) If the resolved components of the displacement, perpendicular to the line of discontinuity and lying individually in the surfaces, are δT_1, δT_2, δT_3, δT_4, then the system of surfaces is in equilibrium if

$$\sigma_1 \delta T_1 + \sigma_2 \delta T_2 + \sigma_3 \delta T_3 + \sigma_4 \delta T_4 = 0$$

for all possible displacements OO'. That is condition [615]. Since the components of the displacements are actually parallel to the lines OA, OB, OC, OD it appears that this is just the same as the well-known "virtual work" condition for the equilibrium of four coplanar forces which could be conceived to exist in the plane of the paper, with magnitudes σ_1, σ_2, σ_3, σ_4 and with directions along the four lines.* Or for that matter we could consider the system of conceptual forces "swung round" through a right angle so that their directions would be at right angles to the four surfaces as Gibbs conceives them to be drawn; such a change in orientation would not affect their equilibrium, if it existed before the change. Gibbs' Figure 13 is the usual polygon-of-forces diagram drawn on this principle. Now suppose that two masses of the liquids A and C were brought into contact with one another and were found to have a surface tension larger than that represented by the length of $\alpha\gamma$ in Figure 13; the condition represented in Figure 11 would be perfectly stable, since free energy does not tend to increase. If, however, this tension were less than that represented by $\alpha\gamma$, the condition would be practically unstable; but to come to a definite conclusion in that case one would have to go more fully into changes in the several components and potentials in the four homogeneous masses occasioned by the development of the surface represented by $O'O''$. Similar considerations in relation to the diagonal $\beta\delta$ would govern the possible growth of a surface between the masses B and D.

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* The reader must guard against the inference that the surface tensions are really tangential forces in the surfaces. We have already referred on p. 510 of this article to the convenience, but the physical unreality, of this conception.

50. *The Possible Growth of a New Surface at a Point of Meeting of a Number of Lines of Discontinuity*

We might have a system in which there is more than one line of discontinuity, these lines meeting at a point. The latter half of page 289 has a very concise statement about the stability of such a system as regards the development of fresh surfaces at the point. Any reader who is not trained in solid geometry or lacks the power to visualize diagrams in space may require some assistance here. Let us begin with the simplest case of four different fluid masses. In this case there will be six surfaces of discontinuity, and four lines of discontinuity. The easiest way to realize this is to drive three nails into a drawing board, calling them X, Y, Z. Attach three threads to them which can be drawn tight and knotted at a point O above the board. A fourth thread, tied to the other three at O, is stretched tight and tied to another nail U, in a support above O. One can then see that we can have one mass of fluid in the pyramid $OYZU$, one in $OZXU$, one in $OXYU$ and one in $OXYZ$. Let us call these masses A, B, C, D, respectively. The surface between B and C is OXU; between C and A, OYU; between A and B, OZU; between A and D, OYZ; between B and D, OZX; between C and D, OXY. There are four lines of discontinuity OX, OY, OZ, OU. Since the surfaces OXY, OXZ, OXU meeting in the line OX are in equilibrium, three forces having magnitudes proportional to σ_{CD}, σ_{BD} and σ_{BC}, and directions normal to these surfaces, are in equilibrium, and can be represented by the sides of a triangle whose corners we shall name β, γ, δ, the side $\gamma\delta$ representing σ_{CD}, $\delta\beta$ representing σ_{DB}, $\beta\gamma$ representing σ_{BC}. In the same way, if the surfaces OYX, OYU, OYZ meeting in OY are in equilibrium, three forces σ_{DC}, σ_{CA}, σ_{AD} normal to these surfaces can be represented by the sides of a triangle $\delta\gamma\alpha$, where α is a fourth point not in the plane of $\beta\gamma\delta$. The figure $\alpha\beta\gamma\delta$ is a tetrahedron, and it will now be easy for the reader to see that the equilibrium of the other two triads of surfaces, viz., OZX, OZY, OZU and OUX, OUY, OUZ is related in a similar way to the triangles $\beta\delta\alpha$ and $\alpha\beta\gamma$. In short, the tetrahedron $\alpha\beta\gamma\delta$ is a geometrical representation of the whole state of equilibrium if it exists. The six edges of the tetrahedron are perpendicular to the corresponding surfaces and represent by their lengths the six surface tensions. The four sides of the tetrahedron, viz., the triangles $\beta\gamma\delta$, $\gamma\alpha\delta$, $\alpha\beta\delta$, $\alpha\beta\gamma$ are perpendicular to OX, OY, OZ, OU, respectively, and if the tetrahedron $\alpha\beta\gamma\delta$ were drawn with the point O inside it, the four points α, β, γ, δ would be respectively situated in the masses A, B, C, D. It is hoped that in this way the reader may grasp the meaning of the earlier sentences of the paragraph, where the "closed solid figure" is the tetrahedron in our illustration for four masses. (There is a small misprint in the second sentence of the paragraph. Beginning after the second comma of the sentence it should read "the edges to the surfaces of discontinuity, and the sides to the lines in which these *surfaces* meet." Notice that "edge" refers to a line of the representative tetrahedron, and "side" to a triangular face of this tetrahedron; "line" and "surface" are retained for the physical lines and surfaces of discontinuity in the system.) After this is grasped, consider a greater number of masses whose dividing surfaces intersect in pairs in lines all of which meet in one point O. Any group of four masses which have six dividing surfaces between them, say, A, B, C, D can be represented as above by a tetrahedron $\alpha\beta\gamma\delta$. Suppose there is another mass A', which has three dividing surfaces with the masses B, C, D, but has no dividing surface with A, having only the point O in common with A. The condition for equilibrium of these surfaces is bound up with a tetrahedron $\alpha'\beta\gamma\delta$ where α' is on the opposite side of $\beta\gamma\delta$ to α. All the edges of this double tetrahedron will have the right directions and lengths to correspond to the surfaces and their tensions. If now a new surface were to develop at O between A and A' and to be in equilibrium, the normal to this new surface would be parallel to $\alpha\alpha'$ and the tension of the surface AA' would be represented by $\alpha\alpha'$, so that for stability with respect to such a formation the tension of the surface between two masses of A and A' would have to be greater than that represented by $\alpha\alpha'$.

51. Some General Ideas and Definitions Concerning the Possibility of a New Homogeneous Mass Being Formed at a Line of Discontinuity or at a Point of Concurrence of Such Lines

Of course bulk phases might develop at a line of discontinuity or at a point where such lines meet. Gibbs considers the first of these possibilities in the subsection beginning on page 289, the second in the subsection beginning on page 297. The argument in each case runs on very much the same lines as in the treatment in pages 258–264 of the possible formation of a new phase between two phases, although it might not appear so on first reading. We shall recast the argument in pages 289–297 so as to bring out this feature.

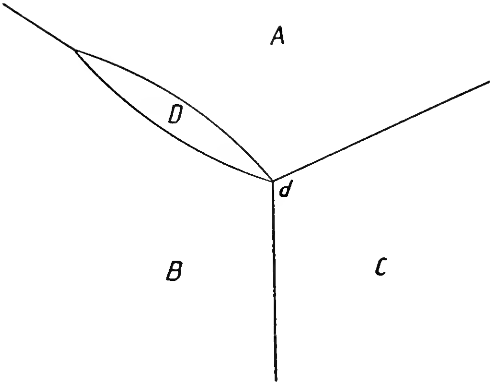

Fig. 6

First of all there must be certain relations between the surface tensions in order that the problem may not be trivial. In the first instance $\sigma_{BC}(t, \mu)$, $\sigma_{CA}(t, \mu)$, $\sigma_{AB}(t, \mu)$, must satisfy conditions of equilibrium, which necessitates any one of them being less than the sum of the other two. Now we assume that we know of a phase D and that we know for it the functional forms of $\sigma_{AD}(t, \mu)$, $\sigma_{BD}(t, \mu)$, $\sigma_{CD}(t, \mu)$ as well as $p_D(t, \mu)$. The values of σ_{BC}, σ_{CA}, σ_{AB} determine the angles at which the surfaces B–C, C–A, A–B meet where no phase D exists. If the phase D is formed and is in equilibrium, σ_{AD}, σ_{BD}, σ_{AB} will have to satisfy certain conditions; so also will $\sigma_{BD}, \sigma_{CD}, \sigma_{BC}$, and $\sigma_{CD}, \sigma_{AD}, \sigma_{CA}$. For instance, if $\sigma_{AB} > \sigma_{AD} + \sigma_{BD}$ no formation of D would take place naturally; the problem of stability as regards formation of D is settled at once. Thus for a problem to exist at all we must postulate

$$\sigma_{BC} \leqq \sigma_{BD} + \sigma_{CD},$$

$$\sigma_{CA} \leqq \sigma_{CD} + \sigma_{AD},$$

$$\sigma_{AB} \leqq \sigma_{AD} + \sigma_{BD}.$$

If now it happened to be true that $\sigma_{AB} = \sigma_{AD} + \sigma_{BD}$ we might have the formation of D as a film between A and B, as in Figure 6. This would resemble the similar cases dealt with on pages 259–264 of Gibbs; the film would form if p_D were greater than a certain critical pressure

$$\frac{\sigma_{AD}p_A + \sigma_{BD}p_B}{\sigma_{AD} + \sigma_{BD}}.$$

If $\sigma_{AB} < \sigma_{AD} + \sigma_{BD}$ we would not have formation of D in this way even in a lentiform mass, the argument being once more that of pages 259–264. But taking the tension conditions to be

$$\sigma_{BC} < \sigma_{BD} + \sigma_{CD},$$

$$\sigma_{CA} < \sigma_{CD} + \sigma_{AD},$$

$$\sigma_{AB} < \sigma_{AD} + \sigma_{BD},$$

we may consider the possibility of the mass D forming as a filament of triangular section stretching along the direction of the original line of discontinuity. If the three pressures p_A, p_B, p_C were equal, the sections of the surfaces B–C, C–A, A–B by the plane of the paper would be straight lines, as in Figure 14 of Gibbs, *da*, *db*, *dc* being the continuations of these lines. If the pressure p_D happened also to be equal to p_A (or p_B or p_C) the sections of the surfaces A–D, B–D, C–D by the paper, i.e, the lines *bc*, *ca*, *ab* would also be straight; but if $p_D \neq p_A$ the surfaces A–D, B–D, C–D will be cylindrical with their generating lines perpendicular to the plane of the paper (Fig. 7). Thus the lines *bc*, *ca*, *ab* will be circular with their convexity outward if $p_D > p_A$, but with their convexity inward if $p_D < p_A$. In general however p_A, p_B, p_C would not be equal, and in that case the lines *da*, *db*, *dc* with their continuations would be curved also, and the convexity or concavity of any of the lines *bc*, *ca*, *ab* would be determined by the conditions as to whether $p_D > p_A$ or $p_D < p_A$, etc. If $p_D = p_A$; of course *bc* is straight. (To avoid awkward digression later we deal with a few geometrical facts now. The *total curvature* of a limited curved line is the exterior angle between the tangents at its extreme points and is equal to the sum of the two angles between the chord joining these points and the tangents. The angles of a curvilinear triangle are the angles between the pairs of tangents drawn to pairs of adjacent sides where they meet. It will be easily seen that the excess of the sum of the angles of a curvilinear triangle over two right angles is equal to the *algebraic* sum of the total curvatures

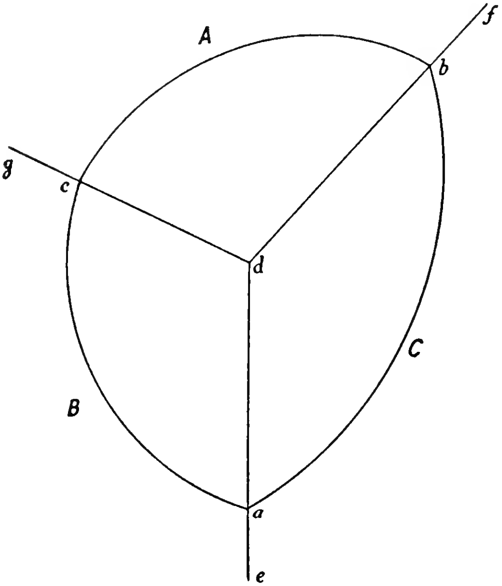

FIG. 7

of its sides, the curvature being reckoned positive for a side if it is convex outwards, negative if concave. On account of this convention of signs it will be seen that the excess may be positive, negative or zero, showing that it is possible for a curvilinear triangle to be like a rectilinear in having the sum of its angles equal to two right angles.) If now a mass of the phase D can exist in equilibrium there is an equilibrium for each of the three triads of tensions at each of the new lines of discontinuity; there is also an equilibrium for the triad of tensions at the original line of discontinuity whose section by the paper is d. We construct a rectilinear triangle whose sides represent the magnitudes σ_{BC}, σ_{CA}, σ_{AB}. Its angles must then be the supplements of the angles between the tangents (or normals) at d; so we can set it in such an orientation that its sides are parallel to the normals at d. This is the triangle $\alpha\beta\gamma$ of Figures 15 and 16 of Gibbs. On $\beta\gamma$ we can construct a triangle $\beta\gamma\delta'$ whose sides represent the magnitudes σ_{BC}, σ_{CD}, σ_{DB}; its angles must be the supplements of the angles between the tangents or normals at a. (The sides of this triangle are not parallel to the normals to the surfaces at a unless da is a straight line.) Similarly we can construct triangles $\gamma\alpha\delta''$ and $\alpha\beta\delta'''$. There are various ways in which the lines $\alpha\delta''$, $\alpha\delta'''$, etc. can fall. If the lines da, db, dc are straight and abc a curvilinear triangle convex inwards, they fall as in Gibbs' Figure 16; if convex outwards they fall as in Figure 8 of this text. Another case is shown later in Figure 9. Only in special cases when the angles of the triangle abc are

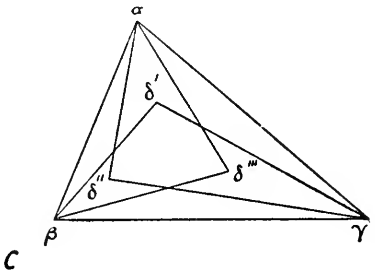

FIG. 8

together equal to two right angles (not necessarily confined to rectilinear triangles) can the situation for equilibrium be represented as in Gibbs' Figure 15. The case represented by Figure 16 is said by Gibbs to be one in which the tensions of the new surfaces "are too small to be represented by the distances of an internal point from the vertices of the triangle representing the tensions of the original surfaces," as is the case in Figure 15. The cases represented in Figures 8 and 9 of this text are said to be of the type in which the tensions of the new surfaces are too large to be represented as in Gibbs' Figure 15.

52. The Stability of a New Homogeneous Mass Formed at a Line of Discontinuity. A Summary of the Steps in the Argument

Having laid down these general ideas and definitions Gibbs proceeds to the argument concerning the stability of a mass formed in this way. It is long and detailed, covering more than four pages, and it may be well for the reader first to glance through a summary of the steps, with certain details left out which can be filled in later. (In following such details at first, one is apt to lose the thread of the argument.)

The first step is on page 292 and concerns equilibrium, stable or not. It is shown that if W_S and W_V are the two quantities defined in [626] and [627] then if the system is in equilibrium

$$W_S = 2W_V.$$

(Notice that a similar type of numerical relation holds for cognate quantities in cases of equilibrium treated previously. See equations [563], [564], [569] of pages 260, 261.) It is also shown that for equilibrium the quantity $W_S - W_V$ must be at a maximum or minimum value as compared with any configuration (equilibrium or not) of the surfaces adjacent to the equilibrium configuration, i.e., so long as tensions and pressures are maintained unchanged at the values corresponding to the temperature and potentials throughout the system.

In the second step it is shown that, since for stable equilibrium $W_S - W_V$ must be at a minimum value as compared with adjacent configurations, there is instability if W_V is a positive quantity (and therefore also W_S, since $W_S = 2W_V$). If W_V is negative the system is stable. (One can hardly say that this is "shown." It can be inferred from the proposition that $W_V \propto W_S^2$, proved on page 293, but the inference is not an obvious one; and on the face of it there appears to be a puzzling contradiction between this proposition and [633]. The contradiction, of course, is only apparent; but the reader is asked to defer these difficult points until later and to proceed along the general line of argument.)

The third step shows how these ideas are to be applied to any given set of circumstances. If the pressures and tensions are known, the figure *abcd* can be constructed for the appropriate configuration of equilibrium, if it exists. For since the relative magnitudes of the tensions determine all the angles round the points *a*, *b*, *c*, *d* we can find the angles of each of the curvilinear triangles *bcd*, *cad*, *abd*, *abc*. Also since $p_D - p_A = 2\sigma_{AD}/r_{AD}, \ldots, p_B - p_C = 2\sigma_{BC}/r_{BC}, \ldots$, we can calculate the six radii of the curvilinear sides. The angles and radii are sufficient data to construct the various triangles, if they are consistent with the possibility of a construction; if they are not, of course no such equilibrium configuration exists, and the problem of stability does not arise. If the construction is possible it shows us that the relative magnitudes of the quantities v_D, v_A, v_B, v_C (which are the areas of the curvilinear triangles *abc*, *bcd*, *cad*, *abd*; i.e., the volumes of the mass *D* per unit length normal to the plane of the paper, and the parts into which it is divided by the surfaces *B–C*, *C–A*, *A–B*) can be determined. These can therefore be taken as known in terms of the tensions and pressures. An inspection is now made of the quantity

$$\frac{v_A p_A + v_B p_B + v_C p_C}{v_D}.$$

If the pressure p_D is greater than this it is obvious that W_V as defined in [627] is positive, and from the second step the equilibrium of the mass *D* is unstable so that a disturbance producing a small increase in it would result in a tendency for it to increase still further. If it so happened that this volume v_D were small enough it would mean that the equilibrium of the line of discontinuity at d, without any formation of the phase D, would be at least practically unstable; for if a small filament of the phase D should be formed a little greater than v_D in size per unit length the formation of more of the phase would tend to occur. On the other hand, if p_D happened to be less than the expression written above, W_V would be negative, and the equilibrium of this filament of the phase D would be stable; any small disturbance increasing it would not tend to cause further growth but the filament would tend to return to its equilibrium size. Were v_D small enough this would be tantamount to saying that the equilibrium of the original line of discontinuity was stable. On pages 294–296 Gibbs goes into more detail concerning this for each of the three special cases where the tensions can be represented as in his Figure 15, or are too small to be so represented, or are too large.

53. The Details of the Argument Omitted from the Summary in (52)

Let us now return and fill in the omitted details. We know from earlier parts of Gibbs' treatise that when the values of temperature and potentials remain constant, so that all the tensions and pressures are determined, the equilibrium of any configuration is determined by the test that for *any* deformation of the configuration to an adjacent configuration, equilibrium or not, the variation

$$\Sigma\sigma\delta s - \Sigma p\delta v = 0,$$

and if the equilibrium is stable the variation

$$\Sigma\sigma\Delta s - \Sigma p\Delta v > 0,$$

which means that *for given values of the tensions and pressures* the quantity

$$\Sigma\sigma s - \Sigma pv$$

is a minimum for a stable configuration of the surfaces and volumes. (For convenience we denote the points where the lines in which the section by the paper cuts the exterior envelop of the whole system by the letters e, f, g.) Then

$$\Sigma\sigma s = \sigma_{AD}\cdot bc + \sigma_{BD}\cdot ca + \sigma_{CD}\cdot ab + \sigma_{BC}\cdot ae + \sigma_{CA}\cdot bf + \sigma_{AB}\cdot cg,$$

since the lengths of the curvilinear lines bc, ca, ab, ae, bf, cg, are equal to the areas of the respective cylindrical dividing surfaces for that part of the system which lies between two sections unit distance apart. Also

$$\Sigma pv = p_A\cdot fbcg + p_B\cdot gcae + p_C\cdot eabf + p_D\cdot abc.$$

Now let us subtract from $\Sigma\sigma s - \Sigma pv$ the quantity

$$\sigma_{BC}\cdot de + \sigma_{CA}\cdot df + \sigma_{AB}\cdot dg - p_A\cdot fdg - p_B\cdot gde - p_C\cdot edf$$

which is unchanged in value by any variation of the surfaces A–D, B–D, C–D. The result of this subtraction is

$$\sigma_{AD}\cdot bc + \sigma_{BD}\cdot ca + \sigma_{CD}\cdot ab - \sigma_{BC}\cdot ad - \sigma_{CA}\cdot bd - \sigma_{AB}\cdot cd$$
$$- (p_D\cdot abc - p_A\cdot bcd - p_B\cdot cad - p_C\cdot abd).$$

This is the quantity $W_S - W_V$ of page 292, and since it differs from $\Sigma\sigma s - \Sigma pv$ by a quantity which is unaltered by any variation of the surfaces A–D, B–D, C–D, it is also a minimum for a stable configuration provided the tensions and pressure are given. This leads directly to Gibbs' equation [629]. In order to grasp what Gibbs is doing in the subsequent portion of page 292, let us consider what would happen to the equilibrium configuration which involves a mass of the phase D were the six functions $\sigma_{BC}(t,\mu)$, ... $\sigma_{AD}(t,\mu)$ to be changed to slightly different functions of t, μ_1, μ_2, ..., say $\sigma_{BC}'(t,\mu)$, ... $\sigma_{AD}'(t,\mu)$, while the pressures still retained the same functional forms as before. This would involve a slightly different configuration, causing a change in the areas to $s_{BC} + ds_{BC}$, ... $s_{AD} + ds_{AD}$, and in the volumes to $v_A + dv_A$, ... if equilibrium is to be preserved. For this configuration we should have

$$W_S' = \sigma_{AD}'(s_{AD} + ds_{AD}) + \ldots - \sigma_{BC}'(s_{BC} + ds_{BC}) - \ldots$$

$$W_V' = p_D(v_D + dv_D) - p_A(v_A + dv_A) - \ldots,$$

so that

$$(W_S' - W_S) - (W_V' - W_V) = (\sigma_{AD}' - \sigma_{AD})s_{AD} + \sigma_{AD}' ds_{AD} + \ldots$$
$$- (\sigma_{BC}' - \sigma_{BC})s_{BC} - \sigma_{BC}' ds_{BC} - \ldots$$
$$- p_D\, dv_D + p_A\, dv_A + \ldots$$

or, at the limit,

$$dW_S - dW_V = \sigma_{AD}\, ds_{AD} + s_{AD}\, d\sigma_{AD} + \ldots$$
$$- \sigma_{BC}\, ds_{BC} - s_{BC}\, d\sigma_{BC} - \ldots$$
$$- p_D\, dv_D + p_A\, dv_A + \ldots$$

But since [629] is true for any small change in the configuration it is true for the change indicated by ds_{BC} etc., so that

$$\sigma_{AD} \cdot ds_{AD} + \ldots - \sigma_{BC} ds_{BC} - \ldots$$
$$- p_D\, dv_D + p_A\, dv_A + \ldots = 0,$$

and from this it follows that

$$d(W_S - W_V) = s_{AD} d\sigma_{AD} + \ldots - s_{BC} d\sigma_{BC} - \ldots$$

which is equation [630]. Now this change in $W_S - W_V$ accompanies small changes in the functional forms which express σ_{BC}, etc. in terms of t, μ_1, μ_2, ... but not in the forms for p_A, etc. Suppose these changes to be of such a nature that the tensions all diminish in the same ratio, the pressures of course not altering. Since

$$p_D - p_A = \frac{\sigma_{AD}}{r_{AD}}, \quad p_B - p_C = \frac{\sigma_{BC}}{r_{BC}}, \text{ etc.,}$$

and

$$p_D - p_A = \frac{\sigma_{AD}'}{r_{AD}'}, \quad p_B - p_C = \frac{\sigma_{BC}'}{r_{BC}'}, \text{ etc.,}$$

it appears that

$$r_{AD}' : r_{AD} = \sigma_{AD}' : \sigma_{AD},$$
$$r_{BC}' : r_{BC} = \sigma_{BC}' : \sigma_{BC},$$
$$\text{etc.}$$

Thus the figure representing the configuration would shrink so that the lengths of the lines in the figure would be proportional to the changing values of the tensions; therefore

$$\sigma_{AD}' : \sigma_{AD} = (s_{AD} + ds_{AD}) : s_{AD}$$

or

$$(\sigma_{AD} + d\sigma_{AD}) : \sigma_{AD} = (s_{AD} + ds_{AD}) : s_{AD},$$

and so

$$s_{AD}\, d\sigma_{AD} = \sigma_{AD}\, ds_{AD}.$$

Hence

$$d(\sigma_{AD}\, s_{AD}) = 2s_{AD}\, d\sigma_{AD},$$

etc.

Thus it appears that

$$\begin{aligned} d(W_S - W_V) &= \tfrac{1}{2}\, d(\sigma_{AD}\, s_{AD} + \dots - \sigma_{BC}\, s_{BC} - \dots) \\ &= \tfrac{1}{2}\, dW_S. \end{aligned}$$

Since $W_S = 0$ when $W_V = 0$, it follows that

$$W_S - W_V = \tfrac{1}{2}\, W_S$$

or

$$W_S = 2W_V.$$

This disposes of the details in the first step. Turning to the second we again consider a variation of the type just considered from the equilibrium configuration, i.e., such that the new figure $a'b'c'd$ remains similar to $abcd$. This varied configuration is of course not one of equilibrium for the actual tensions and pressures, but this is of no importance as regards the conditions of equilibrium and stability of the unvaried configuration; W_S' and W_V' can be reckoned for this varied configuration, but of course W_S' is *not* equal to $2W_V'$ since this configuration is not one of equilibrium; actually W_S' involves the same σ_{AD}, etc., as does W_S, but a different s_{AD}; in fact

$$\frac{W_S'}{W_S} = \frac{s_{AD}'}{s_{AD}} = \frac{s_{BC}'}{s_{BC}} = \text{etc.}$$

On the other hand

$$\frac{W_V'}{W_V} = \frac{v_A'}{v_A} = \frac{v_B'}{v_B} = \frac{v_C'}{v_C} = \frac{v_D'}{v_D}.$$

Hence on account of the similarity of the figures

$$\frac{W_V'}{W_V} = \frac{W_S'^2}{W_S^2}.$$

(As mentioned earlier there is no contradiction here with [633] since $W_S' \neq 2W_V'$.) Expressed in another way

$$\frac{W_V + \Delta W_V}{W_V} = \frac{(W_S + \Delta W_S)^2}{W_S^2},$$

or

$$\frac{\Delta W_V}{W_V} = 2\frac{\Delta W_S}{W_S} + \left(\frac{\Delta W_S}{W_S}\right)^2.$$

Since $W_S = 2W_V$, it follows that

$$\Delta(W_S - W_V) = -W_V\left(\frac{\Delta W_S}{W_S}\right)^2.$$

Neglecting quantities of the second order $\delta(W_S - W_V)$ is zero, as it should be for equilibrium; but if we retain higher quantities, $\Delta(W_S - W_V) < 0$ if W_V is positive, and $\Delta(W_S - W_V) > 0$ if W_V is negative, since $(\Delta W_S/W_S)^2$ is positive for any sign of ΔW_S. For stable equilibrium $\Delta(W_S - W_V)$ must be positive for all variations; thus a necessary condition of stability is that W_V should have a negative value in the equilibrium configuration. This is the result obtained in the second step. The reader can now probably manage the remaining points on pages 294, 295. Note that on page 294 a well known theorem in the mensuration of triangles is employed, viz., that the area of a triangle whose sides are a, b, c in length is

$$\tfrac{1}{4}[(a+b+c)(b+c-a)(c+a-b)(a+b-c)]^{\frac{1}{2}}.$$

54. *Consideration of the Case When the New Homogeneous Mass is Bounded by Spherical Lunes*

To follow the reasoning in the last two paragraphs of this subsection (pp. 296, 297) one must visualize somehow the form of D in

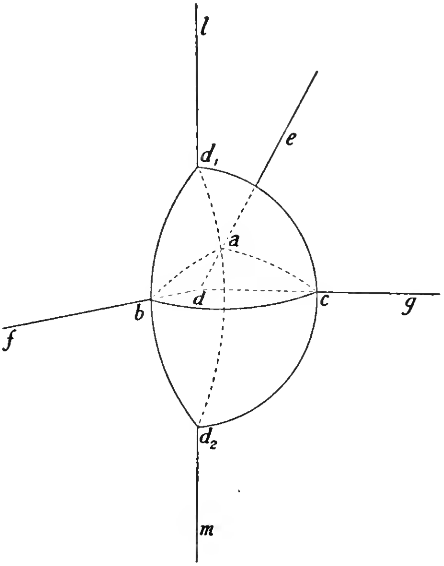

FIG. 9

this case. First imagine (Fig. 9) a thread stretched between two points l and m; mark two points between l and m on the thread and call them d_1 and d_2. The thread represents the original line of discontinuity, and three surfaces B–C, C–A, $A-B$ all containing the thread divide the space round the thread into three portions, each of which contains one of the fluids A, B, C which are supposed to be in equilibrium at these surfaces. Now consider a plane drawn at right angles to the thread with d_1 and d_2 lying on opposite sides of it. Let the thread cut the plane in d, and let de, df, dg be the line sections of the plane by the three surfaces. If a, b, c are three points on de, df, dg, we can conceive an arc of a circle drawn through d_1ad_2 and similarly arcs also drawn through d_1bd_2, d_1cd_2. Further, we can conceive a portion of a sphere (a "spherical lune") drawn so as to connect the arc d_1bd_2 with d_1cd_2, etc. The mass D, if formed, is supposed to be inside the space bounded externally by three such lunes, and the lune joining d_1bd_2 with d_1cd_2 is the surface D–A, and so on. We now name various portions of surface as follows. The lune $d_1bd_2cd_1$ is named s_{AD}, and so on. The portion of the surface B–C which is marked off between the arc d_1ad_2 and the line d_1dd_2 is named s_{BC}. It is in fact the portion of the surface B–C which is, as it were, destroyed by the formation of the phase D. Similar definitions are given to s_{CA} and s_{AB}. Similarly v_D stands for the volume occupied by the phase D and v_A, v_B, v_C for the volumes of the three portions of it originally occupied by the phases A, B, C before the phase D was formed. The discussion of the stability follows the same course as before. Representing the expression

$$\sigma_{AD} \cdot s_{AD} + \ldots - \sigma_{BC} s_{BC} - \ldots$$

by W_S, and the expression

$$p_D v_D - p_A v_A - p_B v_B - p_C v_C$$

by W_V, we have to investigate when $W_S - W_V$ is a minimum or maximum in the assumed state of equilibrium. (Its variation is zero when we neglect higher powers than the first of the variations of the variables.) We can find the ratio of W_S to W_V in an equilibrium state by the same method as before. The only difference in the result is that although, in the changes of size which keep the figure similar to itself, σ_{AD}, σ_{BC}, etc. all vary as the linear dimensions of the figure (since, for instance, $2\sigma_{AD}/r_{AD}$ is to be maintained constant and equal to $p_D - p_A$), the surfaces s_{AD}, etc. vary now as the squares of the linear dimensions. From this it follows that

$$d(\sigma_{AD}\, s_{AD}) = 3\sigma_{AD}\, ds_{AD}$$

so that the analogous result to [632] is

$$d(W_S - W_V) = \tfrac{1}{3}\, d(\sigma_{AD}\, s_{AD} + \ldots - \sigma_{BC}\, s_{BC} - \ldots)$$

$$= \tfrac{1}{3}\, dW_S,$$

and it follows that

$$W_S - W_V = \tfrac{1}{3} W_S.$$

Hence

$$W_S = \tfrac{3}{2}\, W_V$$

$$W_S - W_V = \tfrac{1}{2}\, W_V.$$

In the subsequent steps one need only consider conditions of temperature and potentials for which $p_D(t, \mu)$ is greater than the other pressures. Clearly the figure would not be possible otherwise.

55. The Stability of a New Homogeneous Mass Formed at the Point of Concurrence of Four Lines of Discontinuity

In the last subsection on stability we have to return to the equilibrium considered in the last paragraph on page 289 and to the commentary thereon. Exactly the same principles are applicable as before, and there will be no difficulty experienced in following the argument, once the figure has been visualized. The modification in the thread diagram used in commenting on page 289 can easily be indicated. Above the drawing board used there we place a wire frame in the shape of a tetrahedron *abcd*, with the vertex *d* uppermost and the base *abc* nearest the drawing board. Tie *a* to *X*, *b* to *Y*, *c* to *Z* and *d* to *U*, which is above the frame, by tight threads. We now conceive the phase *D* to be in the space in the truncated tetrahedron *abcXYZ* between the surface *abc* and the exterior envelop of the whole system, and so on. The phase *E* is supposed to form inside the tetrahedron. We are not to suppose that the surfaces *abc*, etc., i.e. *E–D*, etc., are necessarily plane, nor for that matter the surfaces *D–A*, etc. There are ten of these surfaces now, viz. E–A, E–B, E–C, E–D, D–A, D–B, D–C, C–B, C–A, B–A, and when we construct all the triangle-of-force diagrams for the various triads of equilibrating tensions we can fit them together as follows. The original system of A, B, C, D being in equilibrium round a point we can construct a tetrahedron of forces for this equilibrium, as pointed out earlier, and call it $\alpha\beta\gamma\delta$. (It is of course rectilinear.) Now in the new system we have, for instance, at the point a of the system a similar equilibrium existing for the surfaces E–B, E–C, E–D, B–C, B–D, C–D. Hence we can construct a rectilinear tetrahedron of forces for it, and we can arrange three sides of it to coincide with $\beta\gamma\delta$, with the fourth vertex at a point ϵ'. Similarly a tetrahedron $\epsilon''\gamma\delta\alpha$ can be constructed to represent the tensions of the surfaces E–C, E–D, E–A, C–D, C–A, D–A, and one $\epsilon'''\delta\alpha\beta$ to represent the tensions of the surfaces E–D, E–A, E–B, etc., and finally $\epsilon''''\alpha\beta\gamma$ to represent the tensions of E–A, E–B, E–C, etc. In the special case when all the surfaces in the system are plane, the four points ϵ', ϵ'', ϵ''', ϵ'''' coincide at one point ϵ inside $\alpha\beta\gamma\delta$, and the tetrahedron $\alpha\beta\gamma\delta$ can be oriented into a position in which its six edges and the four lines $\epsilon\alpha$, $\epsilon\beta$, $\epsilon\gamma$, $\epsilon\delta$ are normal to the surfaces in the system.

As before, we construct an expression $\Sigma\sigma_p s_p - \Sigma\sigma_n s_n$, where s_p stands for a new surface which has been formed in developing the system with the phase E from the original system without E, and s_n stands for a portion of one of the original surfaces which has disappeared. We call this expression W_S. As before,

$$W_V = p_E v_E - p_A v_A - p_B v_B - p_C v_C - p_D v_D,$$

where v_E is the volume of the phase E, and v_A, etc. the volumes of the parts of it originally occupied by the phases A, etc. We can now prove that $W_S = \frac{3}{2} W_V$; for in this case the preservation of similarity of shape in a conceptually growing phase E would require the tensions to vary with linear dimensions of the figure E (the pressures not changing) while the surfaces s_p, s_n vary as the square of the linear dimensions. The argument proceeds in the now familiar way. If we are considering the stability of the system without the phase E, we need only consider the conditions relating to the system when the amount of phase E formed is very small. In that case, for purely geometrical calculations, we can regard the faces of tetrahedron $abcd$ and also the portions of the surface D–A etc. within it as plane. This means that the tetrahedron $\alpha\beta\gamma\delta$ is similar to $abcd$ and the point ϵ is situated within it just as is the point ϵ within $abcd$ (ϵ is the point which we originally named O). This justifies the various steps in the geometrical argument leading to [641].

XVII. Liquid Films

[Gibbs, I, pp. 300–314]

56. Some Elementary Properties of Liquid Films. The Elasticity of a Film

Since soap solutions are generally used for experimental illustration of the properties of liquid films between two gaseous phases, it may be of advantage to mention briefly some of the most striking facts concerning such solutions. In the first place it is remarkable how great a reduction is produced in the surface tension of water by quite small concentrations of soap. This is, of course, due to the excess concentration of the capillary active soap in the surface layer. Actually, when the bulk concentration of a sodium oleate solution attains 0.25 per cent the surface tension has decreased from about 80 dynes per centimeter to about 30, a figure at which it remains during further increases in concentration. However, it is known that these values are only attained some time after the formation of the surface layer. If the surfaces are continuously renewed nothing like such a lowering of surface tension is observed. Thus Lord Rayleigh obtained for a 0.25 per cent concentration a "dynamic" surface tension equal to that of pure water, as distinct from the "static" value given above. Even a 2.5 per cent solution with a continuously renewed surface recorded 56 dynes per centimeter, or about twice the "static" value. This can only mean that the specific surface layer with the very low surface tension takes some time to form. Some work by du Noüy (*Phil. Mag.*, **48**, pp. 264, 664, (1924)) on extremely dilute solutions shows that concentrations as low as 10^{-5} hardly affect the surface tension initially, but after two hours produce a drop of about one-third in value. This fact should be borne in mind in considering the variations in the tension of soap films which are instanced by Gibbs, and of which many illustrations can be found in A. S. C. Lawrence's book on *Soap films: A Study in Molecular Individuality* (London, 1929).

Of course the thin film between two gaseous phases is not to be regarded merely as a very thin layer. As Gibbs clearly states at the top of page 301, it is in general a *bulk* phase with *two* surfaces of discontinuity each with its appropriate dividing surface and superficial energy or tension. One point must however be noted; owing to its thinness any extension of its area finds no large source of the capillary active substance to draw on so as to maintain the surface layers in the same condition, and the resulting reduction in excess surface concentration produces an increase in the surface tensions and therefore in the combined tensions or "tension of the film." This gives rise to the conception of an *elasticity* of the film, analogous to that of a stretched string or membrane. This will of course have different values according to the conditions imposed, just as occurs in the case of deformable solids. A formula for the value under the conditions prescribed at the bottom of page 301 is worked out by Gibbs on pages 302, 303. In the case of solids or fluids, what is called the "bulk modulus of elasticity" is defined by the quotient of an increase of external uniform pressure on the surface by the resulting decrease in unit volume, i.e., by $-\delta p/(\delta v/v)$. The definition of E in [643] is analogous to this, 2σ being regarded as the tension of the film. If G_1 and G_2 are the total quantities of S_1 and S_2 per unit area, as defined in [652] and [653], then under the conditions prescribed G_1s and G_2s are constant, so that

$$G_1ds + s\,dG_1 = 0,$$

$$G_2ds + s\,dG_2 = 0.$$

These yield [644]. The rest of the analysis on pp. 302, 303 is of a simple mathematical character and can be easily followed. It will be noted that the statement after [655], that E will be generally positive, is based on the assumption that μ_2 in general increases in value with G_2. It is clear that the elasticity is not simply dependent on the thickness of film. The extension must produce some change in the concentration of the components in the actual surfaces of the films, so that in a film held vertically, for instance, the conditions of distribution of the components in successive elements of the film must be different as we move up and down. Draining away of the liquid from the interior of the film does not of necessity cause a change in tension even although the thickness diminishes. The statement in parenthesis at the very bottom of page 303 may be justified as follows. All the other potentials except those of S_1 and S_2 remaining constant, a change in composition with respect to these components produces a change in σ given by

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2.$$

In the argument just preceding we have chosen the dividing surface so that Γ_1 is zero. Then $\Gamma_{2(1)}$ is positive on the assumption that S_2 exists in greater proportion at the surface, as compared with the interior, than S_1. Suppose, however, that we choose the dividing surface so that Γ_2 is zero. This makes $\Gamma_{1(2)}$ negative, and we have of course

$$d\sigma = - \Gamma_{1(2)}\, d\mu_1.$$

But a reduction of S_1 by evaporation, S_2 remaining constant, makes the potential of S_1 diminish so that $d\mu_1$ is negative in value. In consequence $\Gamma_{1(2)} d\mu_1$ is positive and therefore $d\sigma$ is negative.

Pursuing the commentary for the moment, before reference to more recent experimental evidence on these matters than that offered in Gibbs' treatise, we find that on page 305 we meet some remarks on films gradually approaching the tenuity attained by the films which show interference colors by reflected light. The elasticity of a thin film is greater than a thick one as we can see from the equation [650]; for E increases as λ diminishes so long as the interior retains the properties of the matter in bulk, and so the quantities γ_1, $\partial r/\partial \mu_2$, $\partial \Gamma_{2(1)}/\partial \mu_2$ are not different in value for the thick and thin films. This is held by Gibbs to justify his statement near the top of page 305 that, just as the film reaches the limit where the nature of the interior begins to alter, the elasticity cannot vanish and the film is not then unstable with respect to extension and contraction, a statement which has proved to be a remarkably acute prevision of the true state of affairs despite the qualifications of the following paragraph; for quite recent investigation has shown that the thinnest possible film, that showing black by interference, is remarkably stable under proper conditions, and the old idea that thinning necessarily leads to rupture has been disproved.

57. The Equilibrium of a Film

Returning to the thick film, Gibbs shows on page 306 how the mechanical conditions for its equilibrium can be approximately satisfied by regarding it simply as a membrane of evanescent thickness, its plane being placed between the two dividing surfaces of the film according to the rule which connects the line of action of the resultant of two parallel forces with the lines of action of the forces. But the following paragraph shows that such a method of dealing with these conditions of equilibrium is really inadequate, and that the film is not really in equilibrium when it apparently is at rest and the conditions called for by this restricted point of view presumably satisfied. The argument reverts to the equations developed on pages 276–282, and resembles in some particulars the line of reasoning on page 284. Thus according to [612] since the pressure in the film satisfies

$$\frac{\partial p}{\partial z} = - g(\gamma_1 + \gamma_2 + \ldots)$$

it should decrease rapidly with height in a vertical film, yet by [613] if we suppose p' to be the pressure at an interior point and p'' the pressure in one of the contiguous gaseous masses the value of p' anywhere in the film must be between the pressures of the gaseous masses for a film in any orientation, since

$$\begin{aligned} p' - p_a'' &= \sigma_a(c_1 + c_2) + g(\Sigma\Gamma) \cos \theta_a, \\ p_b'' - p' &= \sigma_b(c_1 + c_2) + g(\Sigma\Gamma) \cos \theta_b, \end{aligned}$$

where the suffixes a and b refer to the two faces of the film. This means that in a vertical film both these conditions cannot be established, and in the thick film apparently in equilibrium the liquid is in reality draining away between the faces towards the bottom. As was noted in somewhat similar circumstances on pages 283, 284, there will also be considerable doubt as to the adjustment of the various potentials to equation [617]. If this adjustment took place, then by [98]

$$\begin{aligned} dp &= \gamma_1 d\mu_1 + \gamma_2 d\mu_2 \\ &= -g(\gamma_1 + \gamma_2 + \ldots)dz \end{aligned}$$

since $\mu_r + gz$ would be constant in the film if the condition [617] were true for the rth component. But this is equation [612] which we have just seen cannot hold; so the assumption that [617] is true for *all* the components leads to a contradiction. Thus there must be at least one component for which the condition [617] is not true. It might appear that this requirement could be met if this one component were a component not actually present in the contiguous masses, since then $\mu_r + gz$ in the film for such a component cannot exceed a certain constant M_r, viz., the value of the potential in the gas at the level, $z = 0$, but is not necessarily equal to it. However, as Gibbs points out, one such component is not enough, the situation being similar to one already discussed on page 286. If there were only one such component, it must satisfy equation [617] or else the condition [614] will not be obeyed. For by [508]

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \ldots - \Gamma_r\, d\mu_r,$$

where the suffix r refers to this special component not found in the gaseous masses.
Hence

$$d\sigma = g(\Gamma_1 + \Gamma_2 \ldots + \Gamma_{r-1})dz - \Gamma_r\, d\mu_r.$$

But by [615] (which, unlike [612], must be satisfied even for apparent equilibrium)

$$d\sigma = g(\Gamma_1 + \Gamma_2 \ldots + \Gamma_{r-1} + \Gamma_r)dz,$$

and so

$$d\mu_r = -g\,dz,$$

or $\mu_r + gz$ = constant throughout the film. However, if there are two such components, r and s, a similar line of reasoning will show that

$$\Gamma_r\,d\mu_r + \Gamma_s\,d\mu_s = -g(\Gamma_r + \Gamma_s)dz,$$

which only necessitates that

$$\Gamma_r(\mu_r + gz) + \Gamma_s(\mu_s + gz) = \text{constant},$$

but not two such independent conditions.

In following up the arguments on pages 307–309 the reader may possibly be familiar with Poiseuille's formula for the efflux of liquid from a narrow tube, in viscous flow and under a pressure gradient which is small enough to permit the motion to be zero at the wall of the tube and not to cause turbulent motion. It is

$$m = -\frac{\pi\rho r^4}{8\eta}\frac{dp}{dl},$$

where m is the mass crossing any section in unit time, ρ the density, η the coefficient of viscosity, and dp/dl the pressure gradient along the length l of the tube. This makes the volume of flow per unit time, i.e., m/ρ, proportional to the fourth power of the radius, other things being equal, and this would require a *mean* velocity across a section equal to

$$\frac{\rho D^2}{32\eta}\frac{dp}{dl}$$

(where D is the diameter), and so proportional to the square of the diameter. The formula for the mean velocity of flow between parallel plates at a distance apart equal to D (again for non-turbulent slow motion) is also known to be

$$\frac{\rho D^2}{12\eta}\frac{dp}{dl},$$

or 8/3 times the corresponding Poiseuille value for equal values of D. It is this fact which enables Gibbs to convert Poiseuille's experimental result for tubes into the result [657], somewhat greater than [656], but of the same order of magnitude and sufficiently approximate for the purpose in hand.

Towards the end of the succeeding paragraph there occurs one of those almost casual statements, so common in Gibbs' writings, which have the appearance of extreme simplicity but are not so easy to justify as one might imagine. Somewhat earlier we have shown how the evaporation of S_1, would diminish the tension of the film. (This volume, p. 661, referring to Gibbs, I, 303.) This implies that if we have two elements such that the ratio of the quantity of S_2 to the quantity of S_1 in the first is greater than the corresponding ratio in the second, then the tension in the first element would be smaller than in the second. Suppose the second element to be in equilibrium at the level which it occupies, and that the first element should happen to be situated at the same level. Clearly a small strip of the film lying between this first element and the part of the film immediately above this level would not be in equilibrium. The pull upwards on this strip, which would be balanced by the pull downwards on it if the second element were below it, is greater than the pull downwards on it due to the first element; thus the first element would tend to rise and of course to experience a stretching and have its tension increased.

In the final paragraph of page 309 the observation referred to is now generally known by the name, the "Gibbs ring," and we shall comment on it presently when giving a few details concerning experimental work on films.

Passing on to the middle paragraph of page 310, the writer supposes that the reasoning by which the stated conclusion "may easily be shown" is as follows. We have already seen that a vertical film is not an example of true equilibrium, and although the variation of σ with the height z necessitates variation of some at least of the potentials with z, since equation [508] must be satisfied, the law of variation is not necessarily the genuine equilibrium law [617]. For, if that were valid for all the potentials, p would have to vary with z according to the equation [612], whereas, owing to [613], p is practically constant throughout the interior of the film. The law of variation to which the behavior of the potentials will actually approximate may be worked out in the simple case dealt with in this paragraph. Let S_1 be the water and S_2 the soap, which exists in excess at the surface, so that $\Gamma_2 > \Gamma_1$; we may take it that in the interior $\gamma_1 > \gamma_2$. Since

$$d\sigma = -\Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2$$

and

$$\frac{d\sigma}{dz} = g(\Gamma_1 + \Gamma_2),$$

it follows that

$$\Gamma_1\mu_1 + \Gamma_2\mu_2 + (\Gamma_1 + \Gamma_2)gz = \text{constant.}$$

Moreover, since the pressure is practically uniform throughout the interior

$$\frac{dp}{dz} = 0,$$

and so by [98]

$$\gamma_1 \frac{d\mu_1}{dz} + \gamma_2 \frac{d\mu_2}{dz} = 0$$

or

$$\gamma_1\mu_1 + \gamma_2\mu_2 = \text{constant.}$$

From these two equations in μ_1 and μ_2 we can eliminate μ_2 and obtain

$$(\Gamma_1\gamma_2 - \Gamma_2\gamma_1)\mu_1 + \gamma_2(\Gamma_1 + \Gamma_2)gz = \text{constant.}$$

Since by our assumptions the coefficient of μ_1 in this is essentially negative while that of z is positive, it follows that μ_1, the potential of the water in the film, increases as we rise. On the other hand in the atmosphere the potential of the water will fall according to the usual equilibrium rule [617]. As they are supposed to be equal at the midway level it follows that above that level the potential of the water in the film is greater than that in the atmosphere and there the water will escape into the atmosphere from the film, with the reverse process occurring below. Following a similar line of argument the reader will now find that the subsequent statements on page 310 are not difficult to verify.

The material in pages 312, 313 will be referred to in the brief account of experimental work on soap films which follows.

58. Foams. The Draining of a Film. The "Gibbs Ring"

Apart from the blowing of soap bubbles the most common illustration of the existence of liquid films is to be found in foam, which is really a collection of bubbles of various sizes which coalesce according to the following simple rule: when three films meet they intersect in a line and their planes are equally inclined, i.e., at an angle of 120°. Six such films can meet at one point with the four common edges also passing through this point in a manner which we have already discussed at an earlier stage of the commentary. Thus in the interior of the foam each bubble is bounded by hexagonal plane faces (in general irregular hexagons). The pressure of the confined gas is everywhere the same. Only the outer faces between the foam and the atmosphere are curved to any extent, and only at these faces is there any difference of pressure on the two sides. The whole mass quickly drains to the "black stage" by the interconnected liquid channels. The existence of foam indicates the presence in the liquid of capillary active substances such as saponin. Such substances are to be found in many plants, and the occurrence of stable foams is very marked on that account in tropical rivers.

Actually the line of intersection of three films is not a "line" but a channel of finite cross-section which is in the form of a curvilinear triangle as in Figure 10, where A, B, C, represent three adjacent bubbles, D being the channel of liquid. On account of the curvature the pressure of the gas in A, B or C is greater than the internal pressure of the liquid in D, while the liquid pressure in the films between *A* and *B*, etc. is practically equal to that in the gas. This state of affairs causes the "suction" referred to by Gibbs on page 309, and the liquid is forced by this excess of pressure from the films into the channels, thus assisting other influences such as gravity in the draining of the films. When a film of soap solution is drawn up from a mass of such solution at the mouth of a cup, we have a ring shaped channel of this kind where the film meets the horizontal surface of the general mass and into this "Gibbs ring" there is a considerable draining of the film by this suction and gravity.

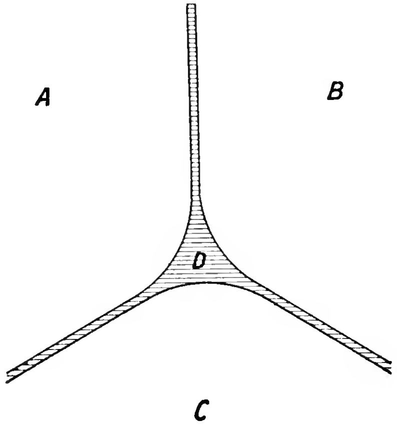

FIG. 10

59. *The Black Stage of a Soap Film*

In general a newly formed soap film passes through a regular succession of changes. Recently, much more light has been thrown on the nature of the succession by improvement in the methods for preventing mechanical shock, sudden large changes of temperature and, more especially, contamination of the solution. In this way it has been shown that the fundamental change is the thinning down to the black stage, so that the black stage is the only film in true equilibrium. It is true that it can hardly be called a stable equilibrium in the accepted sense of stability since the black stage is extremely susceptible to mechanical shock, being much less resistant to this than the thicker, colored films. Nevertheless, with extraordinary precautions soap films have been kept "alive" for many days, and in one case certainly for a year. For further information on the preparation of the solutions and on the experimental technique, the reader can consult Lawrence's book already mentioned.

In a vertical film the black stage appears at the top and gradually spreads downwards, the boundary between it and the thicker film immediately below being quite a sharp horizontal line. In the lower part of the film illumination by monochromatic light shows, by the appearance of horizontal bands of color across the film, that stages of different thickness succeed one another, the whole mass draining all the time and the banded appearance going through characteristic changes accordingly. In a horizontal film the black appears as a small circular disc. The sharp boundary between the black and the adjacent part indicates a change in thickness with a very steep gradient, involving changes occasionally as much as several hundred to one between black and adjacent parts, and never less than ten to one. As stated on p. 662 of this volume, it used to be believed that the appearance of black necessarily led to early rupture of the film, but this is not a fact provided shock and contamination are avoided. The thinning of a horizontal film in this way is of course not due to gravity; actually the Gibbs ring formed where the film meets the solid boundary to which it is attached is responsible for this draining.

We have referred briefly to the normal thinning of a film, under, of course, careful conditions, but certain abnormal developments occur at times, and Gibbs himself knew of these as we see on reading pages 312 and 313. Sir James Dewar made many experiments on vertical films in which he observed that instead of the black spreading steadily over the film, black spots appeared in many places, especially at the thicker parts. These spots rise to the top of the film and there coalesce to produce an apparently normal black film, and the film settles down thereafter to the usual course of development. This so called "critical" behavior of the film seems to require some definite stimulation from external sources to bring the film to the state in which the "critical black fall" begins.

Space permits us to mention only one more point, first clearly established by Perrin, viz., that soap films can be "stratified," the layers of a stratified film being formed by the superposition of identical elementary leaflets in suitable numbers. The thickness of each layer is an integral multiple of an elementary thickness which is of the order of 5 to 6 millimicrons. Actually it is known also that under certain circumstances more than one thickness of black film can be formed; but the thicker blacks do not last long and quickly give place to the thinnest. With this extreme tenuity of the ultimate black film, it becomes porous and the air inside a bubble which has reached the black stage is gradually forced out by the excess of internal pressure, thus leading to the collapse of the bubble. The reader will find a wealth of interesting material in Lawrence's book, with abundant references to original papers on the subject.

XVIII. Surfaces of Solids

[*Gibbs, I, pp. 314–331*]

60. The Surface Energy and Surface Tension of the Surface of a Solid

In the first portion of this subsection Gibbs returns to the treatment of a problem which he has previously considered in pages 193 *et seq.* of the section on the conditions of equilibrium for solids in contact with fluids, viz., the expression of the condition which relates to the dissolving of a solid or its growth without discontinuity. The problem is now studied with regard to the effect of the existence of surface energy on the course of events, a point not raised in the earlier discussion. He defines his terms for surfaces between a solid and a fluid in a manner similar to that employed for fluid interfaces, and it is to be observed that his symbol σ is now definitely associated with surface *energy* and not surface *tension*. We have already referred to common misconceptions in this connection in the case of fluids, where, however, the concept of a surface *tension* may prove serviceable at times as a fiction whose use can be justified by mathematical convenience. But here the various states of strain in a solid can perhaps justify us in the conception of a tension depending on a stretching of the surface arising from a deformation of the solid itself, but this is entirely different from the surface energy. In the case of a fluid the quantity σ, whatever name we give it, is not the measure of the work of a force *stretching* the fluid surface by unit amount but of the increased energy acquired by molecules which have come from the interior of the fluid to form a new unit of surface, the surface itself being otherwise in the same physical condition as before. It may be, as Gibbs remarks, that in certain cases the actual numerical values for the two quantities in the case of a solid approximate to each other, and so, for example, equation [661] can receive an interpretation, as explained in the last paragraph of page 317, which makes its content identical with that of equation [387]. However, the writer has some reservations to make on this matter which will be given presently.

A reminder to the reader may not be out of place when he begins to read this subsection. The words isotropic and anisotropic can be applied to states of stress in solids, as well as to the solids themselves. This matter has been already dealt with in the commentary on "The Thermodynamics of Strained Elastic Solids" (Article K) which may well be referred to in this connection.

On pages 316–320 the equation equivalent to [387], viz. [661], is deduced for isotropic solids. On pages 320–325 crystalline solids are considered. The proof of [661] will offer no difficulty, as the reader will now be familiar with the type of argument employed. One special point alone calls for comment. If a closed curved surface is displaced by an amount δN along its normals so as to take up a new position "parallel" to its original form, each element of its surface, Ds changes in area by an amount $(c_1 + c_2)\delta N Ds$ where c_1 and c_2 are the principal curvatures of the element. This fact, the proof of which will be found in the section on curvature in Article B of this volume, is used in the expression for the increment of energy with which the argument starts and in the subsequent expressions for increment of entropy, etc. Just after equation [661] there occurs a statement concerning the expression $p'' + (c_1 + c_2)\sigma$. This is dependent on the same considerations as were used in our discussion on p. 521 of the connection between the external pressure on the spherical surface of a liquid and its internal pressure at the surface, the quantity $c_1 + c_2$ here replacing the quantity $2/R$ there, R being the radius of the sphere. It is in fact equivalent to the use of equation [500]. The writer, however, feels that the qualification in the text concerning σ being the "true tension of the surface" is uncalled for. If σ is the free surface energy per unit area, the same form of proof will hold as before for the statement, and will lead to the same conclusion, viz., equation [500]. It is true that in the case of the solid the causes giving rise to free surface energy will include changes in the relative configuration of molecules in the surface arising from surface stretching, as well as the already familiar inward attractions of underlying molecules; but whatever be the causes, σ has the same meaning in these formulae as before, and $p'' + (c_1 + c_2)\sigma$ is the internal pressure under all circumstances. On the same grounds the writer is somewhat critical concerning the remarks at the end of the first paragraph on page 318. He feels that the conclusion there drawn is based on a mistaken view that the surface phenomena resemble in this respect those in a stretched membrane separating two bodies of fluid, and he cannot persuade himself that one should adopt any other view concerning σ than those already indicated; if he is right in this contention and if one introduces the conception of an *isotropic internal* pressure, he fails to see how the familiar proof from energy considerations already used on pages 228–229 of Gibbs' work is not as valid as before. In short he cannot satisfy himself that there is any need in these arguments to separate artificially a certain portion of the free surface energy, viz., that arising from stretching apart of the surface molecules, from the whole amount of it, and to introduce it as the sole determining factor in the difference between internal and external pressure.

In order to convince himself of the truth of the statements made in the second paragraph on page 318, the reader should refer back to the conclusions drawn in Gibbs' discussion of strained solids at the bottom of page 196, which might otherwise not be recalled. The additional argument when gravity is taken into account needs no comment.

The gist of the long footnote on page 320 is that since two pieces of ice, for example, do not freeze together spontaneously but only under pressure, the free energy of the discontinuous region formed between the two pieces on freezing, denoted by σ_{II} is not less than, and is most probably greater than, the sum of the free energies of the two surfaces in existence before the regelation, denoted by $2\sigma_{IW}$.

The argument concerning crystalline solids follows the same course. To enable the reader to grasp the reason for the second part of the expression on page 320, Figure 11 is supplied. It represents a section of the crystal at the edge l' which is supposed to extend at right angles to the plane of the paper; BE is part of the section of the surface s by the paper, AB a part of the section of s'; CF is a part of the section of the surface s after growth of the crystal, so that the angle EBC is ω', and CD is equal to δN. The face s' has, as far as the phenomena around the edge at D are concerned, increased by an area $l' \cdot BC$, i.e. $l' \cdot CD$ cosec ω' or $l' \cdot$ cosec ω' δN; the face s has decreased by an area $l' \cdot BD$ or l' cot ω' δN. Of course if ω' is greater than a right angle, at any edge, the term involving cot ω' in the corresponding portion of the summed expression will be essentially negative and the term will be virtually an addition term, as is clear from the fact that at such an edge s increases in area.

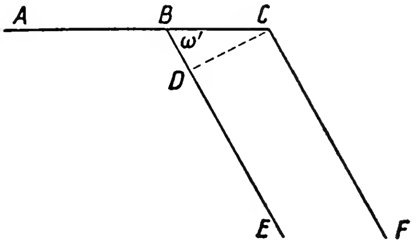

FIG. 11

The argument on page 322 concerning stability follows precisely the same course as those employed earlier in the case of fluids, on which we have already commented fully. It should offer no difficulty. Nor is there anything in the three following pages requiring any special explanation, except perhaps the remark in the footnote on page 325, that the value of the potential in the liquid which is necessary for the growth of the crystal will generally be greatest for the growth at that face for which σ is least. The reader will note that if formation of solid material is taking place on this face, it is the faces with larger values of σ which are increasing in size, and therefore the crystal is receiving greater increments of energy per unit increase of area than would be the case if growth took place on one of the sides of low σ.

It should be mentioned that attempts have been made, especially in recent years, to measure the free surface energy and total surface energy of solids, but with very doubtful success owing to the inherent difficulties of the situation. Owing to the absence of mobility the usual methods applicable to liquids fail. However, one can resort to a method which treats the solubility of small particles as varying with size in the same way as the vapor pressure of small drops of liquid. The method is theoretically sound but there are unavoidable errors in its application. It is known that the vapor pressure, p, of a liquid above a plane surface and p', the vapor pressure in equilibrium with a spherical drop of radius r, are connected by the relation

$$\frac{Rt}{M}\log\frac{p'}{p}=\frac{2\sigma}{r\rho},$$

where M is the molecular weight of the vapor and ρ the density of the liquid. The solubilities of a solid in large bulk, and in the form of small spherical particles, are related in a similar manner. However, there are considerable difficulties in grinding suitable particles, or in preparing them by rapid condensation from vapor or by deposition from solution. It is not probable that the surface atoms in such small portions will have the same regular arrangement as in a plane surface. The reader should consult the following papers for details:

Ostwald: *Z. physik. Chem.*, **34,** 495 (1900).
Hulett: *Z. physik. Chem.*, **37,** 385 (1901).

Hulett: *Z. physik. Chem.*, **47**, 357 (1904).
Dundon and Mack, and Dundon: *J. Am. Chem. Soc.*, **45**, 2479, 2658 (1923).
Thompson: *Trans. Faraday Soc.*, **17**, 391 (1922).

Attempts have also been made to measure the change in total surface energy owing to smallness of particle by determining the heats of solution for small and large particles. See papers by Lipsett, Johnson and Maass in the *J. Am. Chem. Soc.*, **49**, 925, 1940 (1927); **50**, 2701 (1928).

61. Contact Angles. The Adhesion of a Liquid to a Solid. Heat of Wetting

Pages 326, 327 of Gibbs' treatment deal with the derivation from the very general method, used earlier on page 280, of the well-known contact-angle relation [672]. The double relation [673] is necessary for an edge. Thus if the line of meeting receives a virtual displacement from the edge of the solid along the face of *s* in contact with *A* (Fig. 12) so as to allow the liquid *B* to come into contact with unit of area of this face, the interface between *A* and *B* is reduced by an area of amount cos α, where α is the angle *YXP*. (This is in general actually an increase since α is usually obtuse.) Thus there would be a

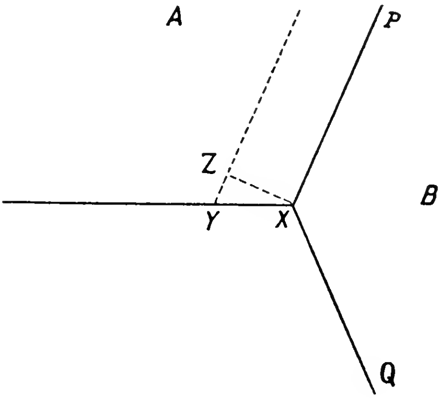

FIG. 12

change of free surface energy of amount $\sigma_{BS} - \sigma_{AS} - \sigma_{AB} \cos \alpha$. For equilibrium this must be positive or zero, and so

$$\sigma_{BS} - \sigma_{AS} \geqq \sigma_{AB} \cos \alpha.$$

Similarly

$$\sigma_{AS} - \sigma_{BS} \geqq \sigma_{AB} \cos \beta,$$

where β is the angle *QXP*. If *A* and *B* are in contact with a single face, α and β are supplementary angles, and the signs of inequality must be removed since the two statements would be contradictory in that case; thus we obtain [672]. A very good account of the measurement of contact angles is given in Adam's book on the *Physics and Chemistry of Surfaces,* Chapter VI, where, in addition to the well-known troubles due to contamination, the effect produced by a movement of the liquid along the surface of the solid is discussed, an effect which is not sufficiently recognized in much of the literature. The contact angle gives a very good idea of the relative magnitudes of the adhesions of different liquids to a given solid. The measure of such an adhesion is the energy per unit area required to separate the solid and liquid from contact. Thus if σ_{LA} is the surface tension of the liquid in contact with air, σ_{SA} that of the solid in contact with air and σ_{LS} that of the interface between solid and liquid, this "work of adhesion" is equal to $\sigma_{LA} + \sigma_{SA} - \sigma_{LS}$. If now α is the contact angle at which the liquid-air interface meets a wall of the solid (measured in the liquid) we have from [672]

$$\sigma_{LA} \cos \alpha = \sigma_{SA} - \sigma_{LS}.$$

Therefore the work of adhesion, being measured as above, is equal to

$$\sigma_{LA}(1 + \cos \alpha).$$

If the contact angle is zero the work of adhesion is equal to $2\sigma_{LA}$, which is the energy required to separate the liquid from itself (since such a separation produces two surfaces in contact with air, where there were none previously), and so if the liquid attracts the surface as strongly as (or indeed more strongly than) itself, the contact angle is zero. On the other hand, an obtuse angle of contact, such as in the case of mercury and glass, indicates relatively small adhesion or absence of wetting. Reference should also be made to the "heat of wetting" in this connection. Heat generally results from the making of a contact between the surfaces of a liquid and a solid. This heat is the *total* energy of the wetting of the solid by the liquid, and is connected with the adhesion or free energy of wetting by the same relation as exists between the total and free energies of a surface, as can be easily shown by combining the three equations derived thus for the three interfaces, solid-air, liquid-air, solid-liquid, with the definition of adhesion given above. In fact if W_{SL} is the work of adhesion, the expression for the heat of wetting per unit area is

$$W_{SL} - t\,\frac{dW_{SL}}{dt}.$$

However, there seems to be considerable difficulty involved in calorimetric determinations of the heat of wetting, as widely divergent results are obtained by different experimenters, although the existence of the phenomenon has been known for over a hundred years. In consequence, the result just quoted has not been verified, since it would require, in addition to a knowledge of the changes of σ_{LA} and α with temperature (which could be obtained with sufficient precision), reliable values of the heat of wetting, which appear to be wanting. The reader should consult Adam's *Physics and Chemistry of Surfaces* and Rideal's *Introduction to Surface Chemistry,* Chapter V, for further information and references. The matters just dealt with are also closely connected with the question of the conditions under which a liquid will spread as a film over a solid, or remain in compact form as a drop. For an adequate treatment of this important point and its bearing on lubrication reference can be made to Chapter VII of Adam's book, as space is not available for more than a passing remark here. In the same volume a brief account is given of the connection between contact angles and the separation of minerals from a mixture by the "flotation" process.

There is of course an "adsorption equation" for a solid-fluid interface; it is [675] of Gibbs, or its equivalent, [678]. Reference to adsorption at a solid surface has already been made earlier in this commentary, where an account is given of Langmuir's deduction of his adsorption equation from statistical considerations. Here the experimental results are once more so difficult to interpret that the situation is far from satisfactory as regards proving or disproving any theory. The reader is once more referred to Adam, Chapter VIII, for an adequate account with references.

XIX. Discontinuity of Electric Potential at a Surface. Electrocapillarity

[*Gibbs, I, pp. 331–337*]

62. Volta's Contact Potential between Two Metals and Its Connection with Thermoelectric and Photoelectric Phenomena

The brevity and caution with which Gibbs refers to these matters is natural when one remembers the date of publication of this memoir. In this connection a letter written to W. D. Bancroft, printed at the end of the volume (Gibbs, I, pp. 425–434), will prove of interest, especially the paragraph at the top of page 429. The situation has been, of course, radically altered since those days, experiment having in the meantime clarified obscurities and removed doubts inherent in any treatment undertaken at that time.

Historically, the question of electrode potentials dates back to Volta's early researches on contact potentials between metals. The discredit into which that hypothesis fell during the nineteenth century was due, of course, to the extreme insistence by the physical chemists and some physicists on the source of the energy transformations in the cell. This led them to look for the source of the E. M. F. of the cell entirely at the metal-electrolyte interfaces, though it must be remembered that Volta's theory was ably defended by many physicists, among whom must be reckoned Lord Kelvin and Helmholtz. An account of the famous controversy will be found in Ostwald's *Elektrochemie, Ihre Geschichte und Lehre,* or in briefer guise in the first few pages of a paper by Langmuir, "The Relation between Contact Potentials and Electrochemical Action" (*Trans. Am. Electrochem. Soc.,* **29,** 125 (1916)). The great temporary success of Nernst's "solution pressure" hypothesis still further intensified the neglect of Volta's ideas. It was the essence of Volta's theory that the contact P.D. between two metals is the difference between two quantities, each one being a characteristic of one metal only, and Volta recognized that such an assumption fitted very simply with the fact that in a closed chain of different metals in series no current flows. It must be admitted that the great discrepancies between the different experimental attempts to measure Volta potentials militated against the success of the theory as a working hypothesis, and led people generally to believe that such potentials, if they existed, were the result of chemical actions at the surfaces of metals and not characteristic of the metals purely and simply.

But today investigation of thermionic and photoelectric phenomena has greatly altered the status of Volta's ideas just when the validity of Nernst's hypothesis is being seriously questioned by the physical chemists themselves. The work initiated by Richardson on thermionic emission, and the great power which experimentalists possess in producing high vacua and maintaining scrupulously the cleanliness and freedom from contamination of metal surfaces, has demonstrated beyond question that electron emission from metals is an intrinsic property of pure metals, and that for each metal there is a characteristic quantity, viz., the energy absorbed when an electron escapes from the metal across the surface. If this be postulated it follows as a logical result that when two metals are in electric equilibrium there must be a P.D. between them if their "electron affinities" are different. (The electron affinity is defined as the quantity ϕ, where $e\phi$ is the characteristic energy of escape referred to, e being the *numerical* value of the electron charge.) Further, the experimental work of Langmuir, Millikan and others has placed the existence of this P.D. beyond the pale of doubt. To demonstrate the logical dependence of contact potentials and electron affinities is not a difficult matter, but it requires the reader to be very clear on certain elementary points in the theory of electricity. Thus the definition of electric potential at a point is given in the words "the work required to bring unit positive change from infinity to the point," but it is not always borne in mind that the transference of the charge is assumed *not to disturb the existing distribution of electric charge in space.* The neglect to take account of this proviso will lead to paradox and perplexity in some cases. Thus suppose we have an uncharged conductor far away from all other conductors so that it is at zero potential. Now imagine the test positive charge to approach the conductor from infinity; as it gets near, a negative charge is induced on the proximate face of the conductor and a positive on the remote; an attraction is exerted on the test charge, which means that work has been done on the charge in coming from infinity to the conductor. Or, if a test charge be taken away from the conductor, the disturbance of the distribution of charge which existed in the conductor *before the test charge was placed near it* will produce an attraction on the charge, and the unwary might therefore infer that the uncharged conductor is at a negative potential, the potential at infinity being taken to be zero as usual; but of course that is an erroneous conclusion and due to neglect of an essential feature of the definition of potential. Another point to be borne in mind (but often overlooked) is that there is no discontinuity of potential between a point in a charged conductor and a point just outside it. The quantity which is discontinuous is the intensity of electric force (which is zero inside a statically charged conductor and equal to $4\pi\kappa$ just outside, where κ is surface density of charge), and this intensity is the gradient of the potential. A geometrical illustration can be observed at a point on a graph where there is a sharp break in the slope. There is no discontinuity in the ordinate y, but one in the slope, i.e., in the gradient of y, viz. dy/dx. If there is a discontinuity in the potential at the surface of a conductor, or at an interface between two conductors, it can only arise owing to a "double layer" of opposite charges, say a positive surface charge and, at a physically small distance further out, a negative charge (either in the form of a surface charge or in a more or less diffuse layer) not actually coincident with the positive charge.

We can now give the theoretical connection between electron affinities and contact potentials quite simply if the reader will recall the few remarks on statistical conditions in subsection (9) of this article. Conceive a metal body to be in a vacuum in an enclosure. Electrons escape from it and gradually the metal will become positively charged. (At room temperatures this process would be very slow, but this does not affect the validity of the calculations which are concerned with the ultimate state of equilibrium, attainable of course at much greater speed at high temperatures.) A state of equilibrium is reached (analogous to that of an evaporating liquid in an enclosed space) when as many electrons return to the metal body as leave it in unit time. There is no difference of potential between the metal and a point just outside, but there does exist a difference between the metal and a distant point, since the metal is charged. Let the electron concentration in the metal be n and that in the space adjacent to the metal surface n'; then we have by a well-known statistical relation

$$\frac{n'}{n} = \exp\left(-\frac{e\phi}{kt}\right)$$

or

$$kt(\log n - \log n') = e\phi.$$

If an electron travels from a point near the surface to a point P in the "space charge" where the potential is V_P, the electron *loses* kinetic energy of an amount $e(V - V_P)$ where V is the potential of the metal body and also the potential at a point just outside it. (It would *gain* that amount if the electron were charged positively.*) This follows from the strict definition of potential; for it is assumed that by the time the electron has travelled a physically small distance from the surface the effect of its "induced charge" (i.e., the corresponding positive charge left unneutralized by its exit) on it has vanished and no further work is done against its motion on that account; that has already been reckoned in $e\phi$ and the movement from the surface to P produces no further disturbance of the surface charge and no practical change in the "electron atmosphere" or "space charge" in the enclosure, which has a very low concentration. Hence by the same statistical rule

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* Observe that e is treated here as a number *without sign*; the numerical value 4.8×10^{-10} of the electron charge.

$$\frac{n_P}{n'} = \exp\left(-\frac{e\{V - V_P\}}{kt}\right)$$

or

$$kt(\log n' - \log n_P) = e(V - V_P).$$

Let us now consider two metal bodies not in contact with one another but inside the same enclosure. When in equilibrium the bodies will be at potentials V_1 and V_2. We then have the following relations

$$kt(\log n_1 - \log n_1') = e\phi_1,$$
$$kt(\log n_1' - \log n_P) = e(V_1 - V_P),$$

and two similar relations for the other metal. It follows easily that

$$\begin{aligned} kt \log n_1 - e\phi_1 - e(V_1 - V_P) &= kt \log n_P \\ &= kt \log n_2 - e\phi_2 - e(V_2 - V_P), \end{aligned}$$

and therefore

$$V_1 - V_2 = \frac{kt}{e}(\log n_1 - \log n_2) + \phi_2 - \phi_1.$$

This relation is not disturbed by bringing the metals into contact; it holds for any relative position of the bodies; when they come into contact the electron concentrations *on their contiguous parts* adjust themselves to produce a double layer consistent with the discontinuity of potential $V_1 - V_2$ across the interfacial boundary. The body with the smaller electron affinity has its normal concentration reduced at the interface thus producing the positive side of the layer there, while the excess electrons go to increase the local concentration in the other body, producing the negative side of the layer. It will be seen that this contact potential $V_C = V_1 - V_2$ depends on temperature. Now long ago Lord Kelvin and Helmholtz in combating the view that Volta potentials could be identified with the Peltier effect, showed that the latter is really dV_C/dt being thus simply the temperature coefficient of the Volta effect. (See for example Lord Kelvin's paper, *Phil. Mag.*, **46**, 82 (1898).) If this is so we see that the Peltier effect, i.e., the "thermoelectric power" of two metals is (k/e) $(\log n_1 - \log n_2)$. But we know that this is very feeble compared to V_C, and there is also evidence from the values of electric conductivities and from recent work on the electron theory of metals that the electron concentrations in different metals are of the same order of magnitude, so that the term (kt/e) $(\log n_1 - \log n_2)$ is negligible. Thus, practically,

$$V_C = \phi_2 - \phi_1.$$

This is the modern formulation of Volta's theory, expressing the contact potential as the difference of two electron affinities, each one a characteristic of its metal.

As regards the production of current, suppose the metals to be in contact at a pair of faces, and bent so as to face each other across a relatively wide gap at another pair. If an ionizing agent were placed near the air gap, ions would be created in the gap and be driven one way or the other by the electric field between the two faces at differing potentials, thus tending to annul the field. If the ionization ceases, the P.D. is restored in the air gap; fresh ionization will create fresh current and so on. It will be observed that the energy of the currents is not obtained from the surface of contact of the metals but from the ionizing agent. This vitiates at once one of the implicit assumptions of earlier generations of workers, viz., that one must look for the source of the E. M. F. at the same place as one finds the source of the energy changes. The function of the electrolyte, as Lord Kelvin always emphasized, is to discharge the charged surface of the plates. It does so by means of the ions arising naturally from its own dissociation. Indeed Volta had vague notions of the same kind, although naturally he could have no prevision, in his time, of modern ideas of dissociation and energy.

Of course this changed attitude towards the Volta effect does not carry with it a denial of the existence of a P.D. at a metal-electrolyte interface; it merely asserts that the metal-electrolyte discontinuities in potential do not account for the whole of the E.M.F. of a cell.

63. Discontinuity of Potential between a Metal and an Electrolyte

As is well known, the hypothesis of Nernst concerning the origin and magnitude of the potential discontinuity at a metal-electrolyte interface has been accepted until recently by most physical chemists as an adequate formulation. Nernst's proof of his formula is thermodynamical, and he deduces the result

$$V_e = \frac{kt}{\nu e}(\log p_s - \log p_0),$$

where p_0 is the osmotic pressure of the ion which is the common component of electrolyte and electrode, p_s its "solution pressure" in the metal, ν the valency of the ion, and V_e the excess of the potential of the electrode *above* that of the electrolyte. The "solution pressure" in the metal cannot be intuitively apprehended like the pressure in a gas, or even like an osmotic pressure, which at all events is open to observation by means independent of all considerations of electrode potentials. It is merely brought into the proof to provide a work term in a usual isothermal cycle when electrons occupying volume v in the metal pass into a volume v' in the solution. The proof is well known and can be found in standard texts (e.g., F. H. Newman's *Electrolytic Conduction*, London, 1930, pp. 184–185). The great objection to the hypothesis is the perfectly monstrous values of solution pressure which must be postulated to make the formula fit the facts. Thus for zinc p_s is almost 10^{19} atmospheres, while for palladium it is about 10^{-36} atmospheres; in the latter case the solution would have to be so dilute round the electrode that a quantity of it as large as the earth would contain two palladium ions at most! With such a huge solution pressure zinc would have to part with over one gram of ions per sq. cm. in order to attain equilibrium when placed in an ordinary solution of a zinc salt; to avoid such an obviously impossible result one has to make *ad hoc* hypotheses concerning the extreme slowness with which equilibrium is reached. It is true that, by abandoning the assumption that ionic atmospheres obey the gas laws, Porter and others have shown that more moderate values for p_s can be obtained; but investigators have of late considered other possible explanations of metal-solution pressure. References to these will be found in Newman's book Chapter VI and Rideal's *Surface Chemistry.* A feature of Nernst's formula is its logarithmic form, in which it resembles the contact potential formula obtained above—indeed Nernst's formula could be obtained by somewhat similar statistical arguments provided the physical environment of the metal were as simple as in the case of contact potentials. Now Rideal (*Trans. Faraday Soc.*, **19**, 667 (1924)) has observed that the order of different metals as regards electron affinities is much the same as the ordinary electromotive order. Nevertheless, the fact that an electrode P.D. depends upon the concentration of the electrolyte shows that it is impossible to interpret such a P.D. entirely in terms of a quantity such as is adequate to account for contact potentials. However, Rideal has derived a formula in which the difference between the electrode potential and the electron affinity of the metal is dependent on its atomic volume. Its form is

$$V_e - \phi = \frac{kt}{ve} f(A),$$

where A is the atomic volume of the metal. Schofield (*Phil. Mag.*, [7], **1**, 641 (1926)), by an argument based on Gibbs' chemical potential of an ion, derives a formula

$$V_e = \frac{kt(\log c - \{k_m - k_e\})}{ve},$$

where c is the concentration of the ion in the solution, k_m a quantity "representing the concentration and environment in the metal" and k_e "represents the environment in the electrolyte". The solution is supposed to be dilute; in stronger solutions log c would be replaced by the logarithm of the activity. This is formally somewhat like Nernst's formula, $k_m - k_e$ replacing the term containing the logarithm of the solution pressure. Butler has derived from a statistical argument the result

$$V_e = \frac{u + kt(\log r + \log a)}{\nu e}$$

where u is the energy change for the transference of one ion from metal to solution, a the activity of the ion in solution and r a small constant characteristic of the metal and depending on the number of metal ions per sq. cm. of the metal surface. (See *Trans. Faraday Soc.*, **19**, 729 (1924)).

All these formulae for electrode potentials exhibit one common feature. They attempt to express the P.D. as the difference of two quantities, one related to the metal and one to the electrolyte, and in that respect they resemble the theoretical result obtained above for a contact potential between metals; but the quantity related to the metal can scarcely be said to be "characteristic" of the metal in the sense that it depends *only* on the metal. Thus consider the formula of Butler; it appears in the proof that u is $w_2 - w_1$, where w_1 is a loss of energy by the ion in travelling from the surface to a certain point in the liquid against the ordinary attractive forces of the solid and adjacent liquid, and w_2 is a similar quantity for a movement from the interior of the liquid to the point. A careful examination of the proof shows, however, that the position of this point would alter with the concentration of the electrolyte, so that w_1 would change with this concentration; and so the quantity related to the metal depends as regards its value on the nature of the electrolyte. But, of course, the simpler state of affairs which holds for metals in a chain could not be true for metals and electrolytes; for if it were, no current would flow in any complete circuit made up of metals and electrolytes, as is true in the case of a complete chain of metals.

64. Gibbs' Comments on Electrode Potentials

Leaving these matters, and turning to a few brief comments on Gibbs' own pages, we meet a statement in a footnote to page 333 to the effect that for a cell with electrodes consisting of zinc dissolved in mercury in different proportions equilibrium would be impossible. For, considering a certain solution, if we slightly alter the relative masses for two constituents but maintain the pressure constant, then dp is zero and so $(m_1/v)d\mu_1 + (m_2/v)d\mu_2$ is also zero; so that if $d\mu_1$ is positive, $d\mu_2$ must be negative, or an increase in μ_1 involves a decrease in μ_2. Hence if $\mu_m' > \mu_m''$ then $\mu_z' < \mu_z''$. Thus it would be impossible for the conditions of equilibrium

$$V' + a_m\mu_m' = V'' + a_m\mu_m'',$$

$$V' + a_z\mu_z' = V'' + a_z\mu_z'',$$

to be true simultaneously.

With regard to paragraph (II), p. 334, a discharged ion going into solution would no longer be related to other components by equation [683]; it would be an independent component with in general an entirely different chemical potential from the charged ion. If there were current flowing, a charged ion would appear to have no definite chemical potential since it would not be in equilibrium, but we would infer by [687] that for small currents its chemical potential, if it were a cation, would increase as it travelled towards the cathode, (if an anion, towards the anode) on account of changing electric potential in the solution. The discharged ion would not be affected by the electric field. However, the paragraph indicates the case of minor interest where the chemical potential might remain unchanged by the discharge. Paragraph (III) introduces the possibility of an equilibrium being effected by absorption of an ion by the electrodes, as in the case of the well known polarizing effect of hydrogen bubbles in a simple copper-zinc cell. The phenomena of polarization and of overvoltage can be studied in standard texts. (See for example Chapter VIII of Newman's book, cited above. Chapter VI of the same work gives a good account of the experimental methods used to measure electrode potentials.)

65. Lippmann's Work on Electrocapillarity and Its Connection with Gibbs' Equation [690]

The paragraph marked (IV) makes a brief reference to electrocapillarity, and in it Gibbs derives equation [689] which, under the conditions that govern the use of the capillary electrometer, reduces to a simpler form without the second term on the right-hand side, and this is shown to be equivalent to [690] which is the well-known equation due to Lippmann. The fact that the tension in an interface between mercury and acidulated water is dependent on the electric conditions was first discovered by Varley (*Phil. Trans.*, **161,** 129 (1871)). Two or three years later Lippmann began a fuller investigation of the phenomenon. He derived the equation which goes by his name, and designed the capillary electrometer to test his conclusions.* The essence of his experiment is the use of an electrolytic cell consisting of sulphuric acid solution and mercury electrodes; the anode has a large surface exposed to the solution, the cathode a very small surface (actually the section of a capillary tube). A current is passed, and if it is not too large the density of the current per unit area of the anode is very small, while the current density at the cathode is so great that the cathode surface becomes highly polarized while little or no effect is produced at the anode surface, and the current is stopped by the reverse E.M.F. set up. A new state of equilibrium is produced which varies as the applied E.M.F. from the external source is increased up to a limit beyond which the current cannot be stopped and equilibrium becomes impossible. The theory which he gave for his results is essentially the theory of a charged surface—purely electrical with no hypothesis as to the physical occurrences at a mercury electrode. A charged conductor like a body of mercury has its charge on the surface. Looking at the surface tension as if it were due to tangential attractions in the surface, the conclusion that a surface charge should reduce the surface tension by reason of the mutual repulsions of its parts is very plausible; but there is no need to resort to this fallacious view of the nature of surface energy. Actually there is at the surface an amount of energy $\sigma_0 s$ due to ordinary molecular causes, where σ_0 is the surface tension with the surface uncharged and s the area of surface, and in addition an amount of electrical potential energy $\frac{1}{2}QV$ where Q is the charge and V the potential of the conductor. (Note that there is no hypothesis of a potential discontinuity of amount V at the surface and a double layer of charge.) Were the form of the conductor to change so as to increase the surface by an amount δs and heat to be supplied reversibly so as to maintain the temperature constant, the increase in the energy due to molecular causes is $\sigma_0 \delta s$, but since the same charge Q is on the surface its surface density will be reduced and there will be a fall in electric potential energy, for further separation of similarly charged particles always involves decrease of potential energy. Hence the actual increase in surface energy at constant temperature is less than $\sigma_0 \delta s$ which means that the surface tension of the charged surface is less than σ_0. The total surface energy is $\epsilon_s(s, V, t)$, a function of area, potential and temperature, and $\sigma(s, V, t)$, the surface tension, is defined in the usual way as $\partial \epsilon_s / \partial s$. A change to a new state of equilibrium with the variables at the values $s + \delta s, V + \delta V, t$ produces a change in the total energy given by

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* *Comptes Rendus*, **76,** 1407 (1873); *Phil. Mag.*, **47,** 281 (1874); *Ann. chim. phys.*, **5,** 494 (1875) and **12,** 265 (1877); *Comptes Rendus*, **95,** 686 (1882).

$$\frac{\partial \epsilon_s}{\partial s} \delta s + \frac{\partial \epsilon_s}{\partial V} \delta V.$$

But this must be equal to

$$\sigma \delta s + V \delta Q,$$

i.e., to

$$\sigma \delta s + V \frac{\partial Q}{\partial s} \delta s + V \frac{\partial Q}{\partial V} \delta V,$$

where $Q(s, V, t)$ is the electric charge on the surface. Hence

$$\frac{\partial \epsilon_s}{\partial s} = \sigma + V \frac{\partial Q}{\partial s},$$

$$\frac{\partial \epsilon_s}{\partial V} = V \frac{\partial Q}{\partial V}.$$

By cross-differentiation

$$\frac{\partial \sigma}{\partial V} + \frac{\partial Q}{\partial s} + V \frac{\partial^2 Q}{\partial V \partial s} = \frac{\partial^2 \epsilon_s}{\partial V \partial s}$$

$$= V \frac{\partial^2 Q}{\partial s\, \partial V}.$$

Therefore

$$\frac{\partial \sigma}{\partial V} = - \frac{\partial Q}{\partial s}.$$

This is the result which Lippmann applied to the cathode mercury surface of his electrometer. In the usual form of the experiment a steady current is established in a potentiometer wire, the positive end of which is attached to the large mercury surface of the electrometer; a wire from the mercury in the capillary tube goes to the travelling contact maker on the potentiometer. As the contact slides away from the positive end towards the negative, so that the potential V of the mercury cathode above the electrolyte is lowered, it is observed that σ at first increases and then, passing a maximum, decreases until a state of affairs is reached at which the polarization of the cathode is unable to prevent a flow of current under the external E.M.F. and equilibrium ceases to be possible. If E represents this applied E.M.F., i.e., the P.D. between the positive end of the potentiometer wire and the contact in any state of equilibrium, then $V = V_0 - E$, where V_0 is the excess of potential of the mercury above that of the electrolyte in the "natural state" (i.e., when the applied E.M.F. is zero); and if E_m is the value of this applied E.M.F. in the state of maximum surface tension, then $V_m = V_0 - E_m$, where V_m is the P.D. between mercury and electrolyte in this state. Since initially $\partial\sigma/\partial E$ is positive, $\partial\sigma/\partial V$ is negative and so $\partial Q/\partial s$ is positive. Now $\partial Q/\partial s$ measures the increase of charge required for unit increase in the area of surface, the potential being kept constant; in other words the charge per unit area; it is also in general a function of s, V, t, just as Q is, and we write it $q(s, V, t)$. Thus initially there is a positive charge on the mercury cathode surface. At the point of maximum σ, where $\partial\sigma/\partial V$ vanishes, q is zero, and on further increase in E, q becomes negative. If we write Lippmann's result in the form

$$\frac{\partial\sigma}{\partial E} = q$$

one sees that it is equivalent to Gibbs' equation [690], although at the first glance it would seem as if there were a difference of sign between the two results; for $V'' - V'$ is the applied electromotive force and so [690] becomes

$$\frac{\partial\sigma'}{\partial E} = -\frac{\Gamma_a'}{a_a}.$$

Since Γ_a'/a_a is the excess ionic charge at the surface, a contradiction apparently arises. This disappears, however, on a little thought; one must bear in mind that Gibbs considered the transport of electricity in terms of ions, e.g., hydrogen ions; these only travel from one discontinuous layer to the other; Γ_a' represents the excess of (hydrogen) ions *in the layer of the electrolyte* adjacent to the mercury represented by the singly accented symbols, i.e., the cathode. Thus, as Gibbs points out, there will be a defect of hydrogen ions in this layer in the natural state, since by his equation Γ_a' is negative if $\partial\sigma'/\partial E$ is positive. This involves a negative charge in this layer which is the counterpart of the positive charge on the mercury surface; for of course the region of discontinuity is uncharged as a whole.

66. *The Double-Layer Hypothesis of Helmholtz*

It was in fact this phenomenon of the double layer of charge which Helmholtz emphasized. Holding as he did decided views in favor of Volta's hypothesis of contact potentials, he pointed out that a discontinuity of potential could only exist between metal and electrolyte for the same reason as between two metals in contact, viz., by a condenser-like action arising from equal and opposite charges segregated in adjacent layers of the two materials.* Assuming that the distribution is actually on the surfaces in analogy to the distribution in an ideal plane condenser, it appears that $Q = csV$, where c is a constant, viz., the capacity of the double-layer condenser per unit area. Hence

$$\frac{\partial Q}{\partial s} = cV$$

and

$$\frac{\partial \sigma}{\partial V} = -cV.$$

Thus

$$\sigma(s, V, t) = \sigma_m - \tfrac{1}{2}cV^2$$

or

$$\sigma(s, E, t) = \sigma_m - \tfrac{1}{2}c(V_0 - E)^2.$$

This leads to two results: (1) that the graph of σ and E should be a parabola; (2) that $E_m = V_0$. The first conclusion is certainly only true in a very limited number of cases, while the second, although it has served for some time as the basis for a method of determining absolute electrode potentials, is unquestionably not exact. It was Helmholtz who suggested the method in question. It consisted in measuring the E.M.F. of a cell with one electrode of mercury and the other of the metal whose P.D. against a given salt was required; the desired P.D. was then calculated on the assumption that the potential at the mercury electrode was that given by the value of E_m, obtained as above. Shortly after, he suggested the use of the dropping electrode, a method based on a similar physical picture of the phenomenon.

67. *Recent Developments in the Thermodynamical Treatment of Electrocapillarity*

Since those days the developments of the theory have been along two main lines. We can do little more than make very brief reference to them in our limited space; so we shall have to be content with giving a few of the most important references and then conclude with some remarks, which, it is hoped, will enable the reader to study these papers more critically than he otherwise might do.

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* *Monatsber. Akad. Wiss., Berlin,* 945 (1881). Cf. A. König, *Ann. Phys. u. Chem.*, **16,** 31 (1882). See also Planck, *Ann. Phys.*, **44,** 385 (1891).

One line of advance has carried forward a formal development of Gibbs' thermodynamic treatment of the phenomena at charged interfaces. Consult for example:

Goüy: *Ann. phys.*, **7,** 129 (1917).
Frumkin: *Z. physik. Chem.*, **103,** 55 (1923).
Frumkin: *Z. Physik*, **35,** 792 (1926).
Frumkin: *Ergeb. der exakt. Naturwiss.*, **7,** 235 (1928).
O. K. Rice: *J. Phys. Chem.*, **30,** 1348 (1926).
Butler: *Proc. Roy. Soc.*, **A, 112,** 129 (1926); **113,** 594 (1927).

A good summary of this work will be found in Chapter VII of Newman's book and in an article contributed by Frumkin to the *Colloid Symposium Annual*, Vol. VII, pp. 89–104.

On the other hand the unsatisfactory nature of the conclusions deduced from Helmholtz's condenser-layer theory of the distribution of the charge, and his lack of suggestions as to the manner in which they would be kept apart, has given rise to theories, based on statistical treatment, of "diffuse layers" of double charge. The interested reader can consult the following papers.

Goüy: *Ann. chim. phys.*, **29,** 145 (1903); **8,** 291 (1906); **9,** 75 (1906).
Goüy: *Ann. phys.*, **6,** 5 (1916); **7,** 129 (1917).
Chapman: *Phil. Mag.*, **25,** 475 (1913).
Herzfeld: *Physik. Z.*, **21,** 28, 61 (1920).
Frumkin: *Phil. Mag.*, **40,** 363 (1920).
Stern: *Z. Elektrochem.*, **30,** 508 (1924).
O. K. Rice: *J. Phys. Chem.*, **30,** 1501 (1926).

This development of theory has been occasioned by the deviation of the ascertained facts from the simple conclusions derived from the combination of Helmholtz's ideas with Lippmann's result. We can only mention here one or two of the most important of these deviations. (In the experimental work the solution in contact with the mercury electrodes is generally saturated with an appropriate mercury salt to ensure that the

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anode surface is unpolarizable. Thus a potassium chloride solution is saturated with mercurous chloride; a sulphate with mercurous sulphate, and so on.) The simple parabolic graph for σ and E is very far from being the rule. Thus while curve I (Fig. 13) shows that an $N/20$ solution of KCl nearly fits a parabola, a similar solution of KI (Curve II) is too steep in its ascending portion; its maximum is lower than that for KCl and corresponds to a larger value of E; beyond the maximum it gradually approaches and merges into the KCl graph. According to the simple Helmholtz view, the mercury in its natural state ought to be higher in potential than the KCl solution by

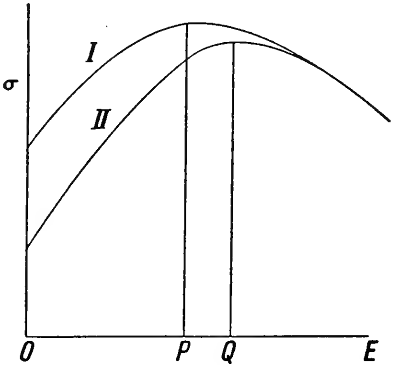

FIG. 13

an amount represented by OP, about 0.6 volt; but higher than the KI solution by OQ, about 0.8 volt. Now if this were so we would expect to find that a cell containing these two solutions with a mercury electrode in each would give a P.D. of 0.2 volt; but it is known that the P.D. is much smaller than this. If then we assume that because the curve is "normal" for KCl there really is a P.D. of 0.6 volt between mercury and KCl in the natural state, we must admit from the evidence of the cell just mentioned that the mercury must also in the natural state be above the KI solution by practically the same amount. Hence, at the maximum state for the latter solution (represented by Q), when according to Lippmann's result the mercury surface has no charge and according to Gibbs (even apart from the fact that the charges in mercury and electrolyte must compensate one another) the electrolyte layer has no excess or defect of ions, it follows that the solution should be higher than the mercury by about 0.2 volt. Of course we cannot be sure that our assumption for the KCl is correct, which only makes matters still more ambiguous; for it is clear that the situation renders doubtful the whole basis of the various methods hitherto employed to measure an absolute electrode P.D.

An explanation for this behavior has been offered on thermodynamic grounds as follows. We have seen that in the natural state positive ions (cations), such as hydrogen ions, will be in defect in the electrolyte layer of the discontinuous region, while negative ions (anions) would preponderate. It is assumed therefore that in this state there are present anions which are capillary-active, in the sense defined in the earlier part of this article; i.e., they tend to lower the surface tension and are "specifically adsorbed" at the surface of the solution on that account. Now, in so far as this has any meaning, it apparently assumes that the negative charge of these adsorbed anions will be to some extent neutralized by the positive charge on the cations in the electrolyte layer. The corresponding positive charge on the mercury will exert the usual depressing effect on the surface tension represented in the Lippmann equation by $-q\,\delta V$. But in addition to this, these anions will exert a still further depressing effect represented by an *additional* term of the Gibbs type $-\Gamma\delta\mu$ (not an equivalent term). Whether this "combination" effect can be derived from a really theoretical treatment we shall consider presently. Of course it is part of the assumed state of affairs that the cations are capillary-inactive and are therefore not "specifically" adsorbed, their presence in the layer is determined by the external electrical influence. Without the specific adsorption of the anions it is assumed that we would have the "normal" parabolic curve; with the adsorption we have an additional depression and the curve begins lower down than the normal. As the E.M.F. rises the electric field drives the active anions out of, and brings inactive cations into, the electrolyte layer, so that the depression of σ below the "normally" depressed value due to the charge grows less; the actual curve gets nearer to the ideal. Even when the exact neutralization of charge is just attained there are still some anions in the layer, balanced as regards charge by cations and, with no charge on the mercury surface, still exerting some depressing effect. At the maximum, the specifically adsorbed anions have nearly disappeared from the layer, so that there are practically only inactive cations with a corresponding negative charge on the mercury, producing a normal depressing effect on the surface tension with a very small specific anionic effect; presently all the anions will have left the layer of solution and thereafter the effect is normal; the curve merges with the ideal curve. It would appear that at the maximum the surface of the mercury should not be uncharged but should have a small negative charge and the electrolyte should be a little above the mercury in potential.

Certain solutions exhibit an opposite effect, producing a curve practically normal to begin with, but falling below the ideal as E increases. This could obviously be accounted for by a hypothesis of active cations with inactive anions. Also there are solutions for which the curve rises like the normal curve, then falls under it and later on merges into the ideal curve once more on its descending branch.

Certain deductions from this view have been verified. Thus, for a solution involving only inactive ions, the P.D. between it and mercury in the natural state should equal the value of E_m; hence if a cell were constructed with mercury electrodes in two such solutions, its E.M.F. should be the difference of the observed values of each E_m. This has been found to be so. Also, if we were to make a cell with mercury electrodes and two solutions each of which involves active anions, we should find that its E.M.F. is equal to the difference between the values of E for the same surface tension provided this value of the tension falls on the normal parts of the graphs in their final descending portions; for at such a stage the specific effect of adsorbed ions has disappeared and only the "purely electric" effect is remaining. This has also been found to be true.

This hypothesis, as we have pointed out previously, involves a combination of a Gibbs term and a Lippmann term in the expression for $d\sigma$, which are not equivalent to one another, but complementary. Thermodynamical deductions of this equation will be found in the references mentioned above. The most complete theoretical treatment is given in Butler's papers in the first list of these references. In the writer's opinion it suffers somewhat by an unnecessary complication, the introduction of a second "surface tension," denoted by γ in the paper. The writer will give a statement of the theory without introducing this additional conception, at the same time making a critical reference to one feature of such proofs.

68. The Reason Why Gibbs' Derivation of His Electrocapillary Equation [690] Exhibits It as Equivalent to Lippmann's Equation

In the first place it may be well to point out once more just exactly how Gibbs' deduction of [690] comes to be *equivalent* to Lippmann's result, and not complementary to it like the "Gibbs terms" in more recent formulae for $d\sigma$. It simply arises from the fact that in Lippmann's proof "electricity" is a "component" of the mercury whose "chemical potential" corresponds to V, the electric potential. We can actually make the proof of Lippmann's result correspond in every mathematical detail to the manner in which Gibbs derives his adsorption equation. Calling ϵ^S the energy of the mercury surface we write

$$\delta\epsilon^S = t\delta\eta^S + \sigma\delta s + V\delta Q$$

as the condition of equilibrium of this surface, V corresponding to μ^S and Q to m^S, the potential and quantity of the component, "electric charge." By the usual reasoning based on the fact that an increase of s requires, for equilibrium conditions at the same t, σ, V, proportional increases in ϵ^S, s, and Q we see that

$$\epsilon^S = t\eta^S + \sigma s + VQ.$$

Hence

$$d\epsilon^S = t\, d\eta^S + \eta^S\, dt + \sigma\, ds + s\, d\sigma + VdQ + Q\, dV.$$

Therefore

$$\eta^s\, dt + s\, d\sigma + Q\, dV = 0$$

or

$$d\sigma = -\eta_S\, dt - q\, dV,$$

i.e., at constant temperature,

$$\frac{\partial \sigma}{\partial V} = -q.$$

Gibbs' own proof just carries through the same steps for the "surface" of the solution, the component being the hydrogen ion whose quantity in the electrolyte is supposed just to neutralize the charge on the mercury (the apparent difficulty about the sign has already been explained) and the chemical potential of the ion is supposed to alter by the amount $\beta\, \delta V$ where δV is the alteration of the electric potential of the solution and β the reciprocal of the electrochemical equivalent a. Let us turn our attention for a moment to this latter assumption.

69. Guggenheim's Electrochemical Potential of an Ion

If one conceives an ion to be transferred from one solution to another (in both of which it is an actual component) across the interface, we can easily prove in the same manner as that in which Gibbs derives his equations [687], [688], that

$$V' + a\mu' = V'' + a\mu'',$$

where the electrochemical equivalent a is a positive quantity for cations and negative for anions. We can write this in the form

$$\mu' + \beta V' = \mu'' + \beta V'',$$

where β is the reciprocal of a, the "chemo-electrical" equivalent as we might call it. Actually it is the quantity $\mu + \beta V$ which is the physically important and significant "intensity factor" in the expression for the energy transferred from one phase to the other by the passage of the mass δm of an ion, viz. $(\mu + \beta V)\delta m$. It appears that in the transfer the division of the energy into two parts $\mu\delta m$ and $\beta V\delta m$(or $V\delta e$) is of no practical importance. The writer need not discuss the point fully here, since the reader can find in a paper by E. A. Guggenheim (*Jour. of Phys. Chem.*, **33**, 842, (1929)) some very interesting remarks on it which will repay careful consideration. We shall consequently replace the expression $\mu + \beta V$ by M, referring to it, as is suggested by Guggenheim in his paper, by the name "electrochemical potential" of the ionic component. This quantity M has equal values in equilibrium conditions for an ion on opposite sides of an interface if the ion is an actual component of both phases. It has of course the same value in the region of discontinuity if it is an actual component of this region. If it exists at the interface and in one bulk phase only, the electrochemical potential has the same value in each, a value which cannot be greater than the value in the bulk phase in which it is only a possible component.

Now it appears on reading parts of the literature that some authors take it for granted that if the electric potential of a phase is altered by the amount δV, then the quantity $\mu + \beta V$ or M must alter by the amount $\beta\ \delta V$. This is no doubt based on an implicit assumption that μ does not change in the meanwhile; but this view seems to the writer to be too narrow and based on the artificial splitting of the real chemical potential of the ion, its electrochemical potential as we call it, into a "purely chemical" and a "purely electric" part, which can vary independently of one another. Even on this physically non-significant analysis, one cannot guarantee that a change in V will not alter the concentration of the ion and therefore the μ of the ion. The truth is, that the only chemical potential of an ion of which we have any direct cognizance is the quantity we have denoted by M, and we actually would have preferred still to use the symbol μ for it, but for the possibility of confusion with the terminology of other writers. In fact, the electric potentials of the phases are now to be reckoned among the thermodynamic variables of the system, and the electrochemical potentials of the ions (although to be quite exact the term chemical potentials should still be used) are dependent on the values of these as well as on the other variables. If a change takes place in the electric potentials *and a new state of equilibrium results,* the M quantities change so as to preserve the same equalities and inequalities as before. The real physical significance of the equivalence of M and $\mu + \beta V$ can be expressed by saying that, if all the electric potentials of the various phases of a system in equilibrium are increased by the same amounts, then the system still remains in equilibrium, no transference of ions (or other components) takes place, and the electrochemical potentials are all effectively unchanged and at their original values. But if the changes of electric potential in the various phases are not equal, no general statement about the changes in the various phases can be made beyond the one concerned with the preservation of equalities, etc., in the case of a varied state of equilibrium.

70. Derivation by Means of the Postulate of "Specific Adsorption" of Ions of an Equation Combining Gibbs' Terms for Ions with a Lippmann Term for Electrons

In accordance with this we write the elementary change of energy in a homogeneous mass in the form

$$\delta\epsilon' = t\delta\eta' - p\delta v' + M_1\delta m_1' + M_2\, \delta m_2' + \ldots,$$

and in a surface in the form

$$\delta\epsilon^S = t\delta\eta^S + \sigma\delta s + M_1\delta m_1{}^S + M_2\, \delta m_2{}^S + \ldots$$

As before, we prove that

$$d\sigma = -\eta_S\, dt - \Gamma_1\, dM_1 - \Gamma_2\, dM_2 - \ldots$$

Since in general each homogeneous mass is uncharged as a whole, and also each surface of discontinuity, it is clear that

$$\Gamma_1\beta_1 + \Gamma_2\beta_2 + \Gamma_3\beta_3 + \ldots = 0,$$

for this expression is the whole charge per unit area on the ions in the region of discontinuity. Hence

$$d\sigma = -\eta_S\, dt - \Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2 - \ldots,$$

which is, of course, the expression Gibbs uses just before [689]. But in reality we can show just as readily that

$$d\sigma = -\eta_S\,dt - \Gamma_1\,dN_1 - \Gamma_2\,dN_2 - \ldots,$$

where N_1, N_2, etc., are any quantities differing from M_1, M_2, etc., by amounts proportional to the various chemo-electrical equivalents. This is in fact one aspect of the statement made above concerning a system which has the electric potentials of all its phases raised or lowered by the same amount.

So far we have considered solutions. If a metal, such as mercury, is one of the phases, then we regard it as a phase with two components, electrons and mercury ions. Now the present theory of metals considers the electric charge of a piece of metal to be measured by the excess of the electrons in it above the positive metallic ions, or the deficiency under; and quite simply the "chemical potential" of the electron is just $\beta_\epsilon V$, where β_ϵ is the chemo-electrical equivalent of an electron, viz., the negative quotient of the electron-charge number by the mass of the electron, i.e., -1.77×10^8. In consequence, if the electrical potential of mercury changes by δV the chemical potential of an electron changes by $\beta_\epsilon \delta V$ or $\delta M_\epsilon = \beta_\epsilon \delta V$. The region of discontinuity between the mercury and the electrolyte is now treated in the usual way. We must, of course, define the position of the ideal dividing surface in order to give a definite meaning to surface excess of any component. Various defining conditions have been employed by different authors. For our purpose the one used by Butler seems to be the simplest; this places the surface so that the excess of mercury ions on the mercury side of the surface is zero, i.e., so that the excess or deficiency of electrons in the mercury measures the electric charge on it; in other words, if Γ_ϵ is the excess of electrons per unit area, q, the electric charge per unit surface, is equal to $\beta_\epsilon \Gamma_\epsilon$.* There may of course be an excess concentration of mercury ions on the electrolyte side of the surface, measured, as usual, by the amount of these ions in excess of the amount that would be in the electrolyte if the concentration of them were the same right up to the surface as throughout the solution. We will denote this excess per unit area by Γ_1. There will of course be other ions present; positive ions such as those of other metals and of hydrogen; negative ions such as sulphion, chlorion, etc. The total charge on all these ions, positive and negative, must be equal and opposite to the charge on the mercury side of the surface, so that if there is a deficiency of electrons in the mercury the negative ions must preponderate in the solution part of the discontinuous region; i.e.,

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* Note that β_ϵ is an essentially negative number.

$$\Gamma_\epsilon \beta_\epsilon + \Gamma_1 \beta_1 + \Gamma_2 \beta_2 + \ldots = 0,$$

where 2, ... refer to ions other than the mercury ions. We now have the equation

$$d\sigma = -\eta_S\, dt - \Gamma_\epsilon\, dM_\epsilon - \Gamma_1\, dM_1 - \Gamma_2\, dM_2 - \ldots,$$

or, at constant temperature,

$$\begin{aligned} d\sigma &= -\beta_\epsilon \Gamma_\epsilon\, dV - \Gamma_1\, dM_1 - \Gamma_2\, dM_2 - \ldots \\ &= -q\, dV - \Gamma_1\, dM_1 - \Gamma_2\, dM_2 - \ldots \end{aligned}$$

This formula exhibits the Lippmann term $-q\,dV$ (q is the charge per unit area *on the mercury*) and Gibbs terms in addition for the various ions present in excess or deficiency on the solution side of the dividing surface. These are the specifically adsorbed ions, cations or anions, whose influence causes the deviations from the simple normal state of affairs covered by the Lippmann term alone. Thus the simple criterion that at the condition for maximum σ the charge should be zero is not necessarily true, since for that condition it is the expression

$$q + \Gamma_1 \frac{\partial M_1}{\partial V} + \Gamma_2 \frac{\partial M_2}{\partial V} + \ldots$$

which is zero. If we assume that δM_1, δM_2, etc., are all altered by $\beta_1\,\delta V$, $\beta_2\,\delta V$, etc., respectively, we would, on account of the fact that $\Sigma\Gamma\beta = 0$, obtain the result that $d\sigma$ is always zero, which is absurd. Or we might assume that some of the M_r's alter by $\beta_r \delta V$ (say the M_1 for the mercury ion because it is a component of the mercury, while assuming that the M_r's of the other ions do not alter). This would require that when $d\sigma$ is zero $q + \beta_1\Gamma_1$ should be zero, and would imply that in this condition the charge on the mercury is just balanced by the electric charge on the excess mercury ions in the solution part of the region of discontinuity, and that there are no anions in this part, or if there are, their charge is neutralized by other cations situated there also. The truth is, however, that such assumptions are not a necessary feature of the analysis. In simple electrostatic theory, a change of electric potential involves a difference of "charge" on the surface of a metal. We make the hypothesis that this is occasioned by excess or defect of electrons. Such electrons are a component of the mercury alone. The mercury ions may travel in or out of the solution across the interface. Other ions do not leave the solution. The change in the concentration of the mercury ions in the solution occasions changes of concentrations in the other ions in the solution, but it does not necessarily follow that these changes produce a change in each M_r which is exactly equal to $\beta_r\delta V$. Indeed, electrocapillary curves constitute the experimental evidence which should enable us to trace the actual changes in the M_r's, had we sufficient knowledge of the distribution of the various ions in the solution layer adjacent to the electrode. It may seem peculiar that changes in the very small region adjacent to the capillary cathode of the electrometer should be responsible for changes in the M_r throughout the whole solution, for of course the M of any ion in the solution must equal its M in the surface layer; but we must not overlook the fact that the electrometer is only part of a complete circuit containing a voltaic cell, and we must not forget the existence of the large mercury anode. It is assumed that it is not polarized, i.e., that its surface has on it the normal positive charge; it is not *electrically* changed. Now this might be quite consistent with a different distribution of ions in the layer of solution adjacent to it; fewer cations and fewer anions in this layer could still provide just the correct negative charge in this layer to balance the unchanged positive charge on the mercury anode. On changing the external E.M.F. by δE $(= -\delta V)$

there is a flow of current for a moment. Electrons go round the external part of the circuit towards the cathode to remove some of the deficiency there; some mercury ions leave the layer adjacent to the anode; some anions enter this layer and, together with some of the anions already present there, are discharged and supply electrons to the mercury anode to maintain the electron flow in the main circuit; for we have supposed that there might be fewer anions as well as fewer cations in this layer and yet the electrical conditions remain unchanged. Thus there would be relatively quite considerable exchanges of ions between this larger layer and the solution, which would occasion differences of concentration and electrochemical potentials in the main body of the solution. This main body would, of course, still be uncharged as a whole, but this again is quite consistent with the existence of fewer cations and fewer anions in it. It is not contended that the physical processes are just those pictured, but the theory must somehow or other justify some changes in the electrochemical potentials of the ions in the main body of the solution if we assume changes in those in the layer of electrolyte adjacent to the cathode, as we clearly do when we assert the validity of an expression such as

$$d\sigma = -q\,dV - \Sigma\Gamma\,dM.$$

One can hardly see how there are to be such changes in the M_r of the ions in the solution if the concentrations are to remain unchanged; and we have just seen that certain changes in concentrations are quite consistent with unchanged purely electric conditions of the solution as a whole and of the anode surface.

71. Some Brief Remarks on the Fundamental Electrical Equations Used by Stern in His Treatment of the Distribution of Ions in a Solution Close to the Cathode of a Capillary Electrometer

It is clear that the electrocapillary curves are insufficient in themselves to unravel the complexities of the situation, without some theory of the distribution of the ions in the layer of solution adjacent to the cathode. This question is dealt with in the second list of references given above. The most exhaustive treatment will be found in the paper by Otto Stern. In the space available the writer can only hope to try to throw some light for the beginner on the fundamental equations used. Regarding the surface of the mercury as the origin from which the distances z of parallel planes in the solution are measured, we represent the electric potential at a plane distant z from the cathode surface by $\psi(z)$, or briefly ψ.* The quantity ψ changes continuously, from the value ψ_0 at the cathode, to zero well out in the solution, i.e., practically at $z = \infty$. If we denote the concentration of a positive ion at z by $C_1(z)$, and of a negative by $C_2(z)$, then the concentrations in the solution are $C_1(\infty)$ and $C_2(\infty)$. These are equal if we adopt as a simple view that there are only two kinds of equi-valent ions, so that we write $C_1(\infty) = C_2(\infty) = C$.

Statistical theory then shows that

$$C_1(z) = C \exp\left[-\frac{F\psi(z)}{Rt}\right],$$

$$C_2(z) = C \exp\left[+\frac{F\psi(z)}{Rt}\right],$$

where F is the numerical value of the charge on a gram-equivalent of ions, and R is the universal gas constant, t being the absolute temperature. Hence the electric charge density ρ at the position z in the solution is given by

$$\begin{aligned}\rho(z) &= F[C_1(z) - C_2(z)] \\ &= FC\left\{\exp\left[-\frac{F\psi(z)}{Rt}\right] - \exp\left[\frac{F\psi(z)}{Rt}\right]\right\}.\end{aligned}$$

In addition to this there is a well-known theorem of Poisson connecting the potential of a distribution of electric charge with the density of this charge. It is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{4\pi}{D}\rho(x, y, z) = 0,$$

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* It has been referred to as V hitherto in conformity with Gibbs' notation. The alteration is made to conform to Stern's symbol.

where $\psi(x, y, z)$ is the potential at the point x, y, z, and D is the dielectric constant of the medium. In the present instance, since ψ depends only on z, this simplifies to

$$\frac{d^2\psi}{dz^2} + \frac{4\pi}{D} \rho(z) = 0.$$

This result is introduced into the previous one and in this way solutions for $\psi(z)$ in terms of z can be found. For details the reader is referred to the literature.

One or two results, however, can be indicated in a general way by means of graphs. Thus suppose we have a graph of $\psi(z)$ before us (Fig. 14), then wherever $\rho(z)$ is positive, $d^2\psi/dz^2$ is negative, i.e., $d\psi/dz$ is decreasing with increasing z, or the slope of the graph is decreasing. (This means, decreasing in the algebraic sense; so that if the slope is negative as in the region OL in the figure, the *numerical* value of the slope is increasing; in the region LM, the slope is increasing algebraically although in the first portion of it the numerical value of the slope is decreasing.) Thus in the figure ρ is positive in the region OL, negative in the region LM and positive once more in the region

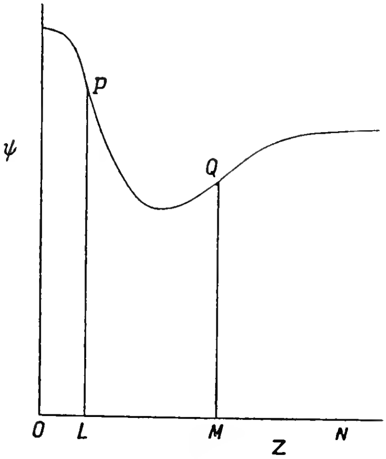

FIG. 14

MN, fading off to zero. P and Q are points of inflection in the curve where the sign of $d^2\psi/dz^2$ changes, that quantity being zero at each of them, so that ρ is zero at the planes L and M. Also, since

$$\frac{4\pi\rho(z)}{D} = -\frac{d^2\psi(z)}{dz^2},$$

it follows that

$$\begin{aligned}\frac{4\pi}{D}\int_0^{z_1}\rho dz &= -\left(\frac{d\psi}{dz}\right)_{z=z_1} + \left(\frac{d\psi}{dz}\right)_{z=0}\\ &= -\left(\frac{d\psi}{dz}\right)_{z=z_1}\\ &= E_1,\end{aligned}$$

where E_1 is the intensity of electric force at the plane L, OL being equal to z_1, and OM to z_2. (It is well known that the electric intensity is measured by the gradient of the potential, and has the direction in which the potential is decreasing. We are assuming the graph to start from zero slope.) Now $\int_0^{z_1}\rho dz$ is the charge per unit area between the planes $z = 0$ and $z = z_1$. Hence this charge is $DE_1/4\pi$. The charge between L and M per unit area is negative and is equal to

$$\int_{z_1}^{z_2}\rho dz,$$

which works out as $D(E_1 + E_2)/4\pi$ *numerically*, where E_2 is the *numerical* value of the intensity of force at the plane M (directed towards the plane at 0.) Finally the charge beyond the plane M is positive and numerically equal to $DE_2/4\pi$. The theory attributes the positive charge $DE_1/4\pi$ to the mercury surface. To do so we imagine that OL is very small and that the graph turns down very suddenly and steeply at first, so that this portion of the graph is really in the mercury. The changes in the solution may be more gradual. The graph we have drawn would suit a picture in which there is a layer of negative ions in the region LM and a layer of (fewer) positive ions beyond it;

this is a picture employed by some writers. The original Helmholtz idea would be pictured by a graph such as that in Fig. 15, curved extremely near the beginning and end of the graph, and a straight steep portion between, sharp bends being the rule at both ends. In the straight portion $d\psi/dz$ does not change, so that $d^2\psi/dz^2$ is zero there and there is no charge; the positive and negative charges are concentrated in extremely thin layers resembling a condenser distribution. The previous graph gives a picture of a practically plane distribution for the positive charge on the mercury surface and a "diffuse layer" of charge in the solution, such as Goüy first suggested. Suggestions have also been made that there may be a diffuse layer in the mercury also.

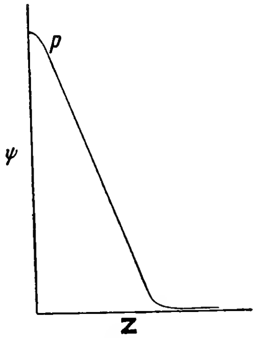

Fig. 15

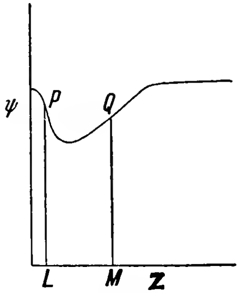

Fig. 16

One last picture (Fig. 16) will show that we might conceive q not to be zero, and yet there might exist no difference of potential between mercury and solution, as the graph has risen to the same level as at the beginning.

M

THE GENERAL PROPERTIES OF A PERFECT ELECTROCHEMICAL APPARATUS. ELECTROCHEMICAL THERMODYNAMICS

[*Gibbs, I, pp. 338–349; 406–412*]

H. S. HARNED

Introduction

THE importance of the contribution of Gibbs to the thermodynamics of galvanic cells resides in the exactness, completeness, and simplicity of his method of treatment. In less than three printed pages, he has set down the complete thermodynamic theory, and has pointed out the fundamental relations between the electromotive force and those basic thermodynamic functions which have proved to be of such immense value to subsequent physico-chemical investigations.

In the following discussion, the thermodynamics of galvanic cells, so far as explicitly treated by Gibbs, will be developed, both by the use of the general functions and by the method of a reversible cycle. Secondly, the arguments of Gibbs regarding the heat supplied to or withdrawn from galvanic cells during their charge or discharge at constant temperature will be presented. In a third section, further ramifications of the theory of this subject not explicitly stated, but contained implicitly in Gibbs' general thermodynamics, will be discussed. Finally, the rôle of Gibbs' fundamental contributions in the subsequent development of the theory of solutions will be briefly outlined.

I. The General Thermodynamics as Explicitly Developed

Certain combinations of two or more pairs of electrical conducting surfaces in electrical contact constitute a galvanic cell. Not all such cells, however, may be subjected to numerical treatment by the methods of thermodynamics, but only those cells which fulfil the following conditions:

(1) No changes must take place without the passage of the current.

(2) Every change which takes place during the passage of the current may be reversed by reversing the direction of the current.

These conditions define the "perfect electrochemical apparatus," or the reversible galvanic cell.

The first condition excludes cells containing metal to liquid surfaces which react chemically, such as Volta's in which alternate copper and zinc plates were separated by a fibrous material moistened with sulphuric acid. The second condition makes possible the measurement of the reversible electrical work of the cell, and, concomitantly, the change in thermodynamic potential, ζ, or the change of work content, ψ, which accompanies the physical or chemical changes occurring in the cell.

Since this second condition is necessary for every direct measurement of changes in ζ or ψ, its more careful consideration, particularly in reference to cell measurement, will help to clarify further discussion. A reversible process is one in which every successive state is a state of equilibrium. The maximum or reversible work is that obtainable from this ideal reversible process. Thus, the evaporation of a liquid against an external pressure just equal to its vapor pressure is a reversible process, and the work done by the vapor is the reversible work.

Let us consider a cell which has proved of considerable importance in recent physical chemistry, and which has the characteristics necessary for the present discussion, namely,

$$\text{Pt} \mid \text{H}_2 \text{ (1 atm.)} \mid \text{HCl } (m) \mid \text{AgCl} \mid \text{Ag}.$$

This consists of a hydrogen electrode, at one atmosphere pressure, in contact with a hydrochloric acid solution at a concentration m, which is also in contact with a silver-silver chloride electrode. All these substances will remain unchanged after the solution has become saturated with the slightly soluble silver chloride. If we connect the terminals, this cell will discharge, positive current will flow from the hydrogen electrode to the silver-silver chloride electrode within the cell, and the chemical changes corresponding to the passage of one faraday of electricity F, when summed up will correspond to the reaction

$$\tfrac{1}{2}\mathrm{H_2}\ (1\ \mathrm{atm.}) + \mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{HCl}\ (m),$$

which will take place from left to right. To measure the reversible electromotive force, E, and the reversible electrical work, NEF, corresponding to the equation of the reaction, the electromotive force of the cell is exactly balanced against an outside electromotive force just sufficient to prevent its discharge and not sufficient to charge it. This is the electromotive force of the cell when no current is passing through the cell, or when the entire system is in equilibrium. If we imagine the cell to discharge against this electromotive force until the quantities specified in the equation have reacted, the cell process will have taken place reversibly. The electrical work, NEF, will then be the maximum, and will be denoted the reversible electrical work.

We shall now follow Gibbs in determining the total energy increase of the cell. Four kinds of changes are possible (Gibbs, I, 338):

"(1) The supply of electricity at one electrode and the withdrawal of the same quantity at the other.
(2) The supply or withdrawal of a certain amount of heat.
(3) The action of gravity.
(4) The motion of the surfaces enclosing the apparatus, as when the volume is increased in the liberation of gases."

In the cell just described, there will be a contraction in volume due to the disappearance of one-half mol of hydrogen at a constant pressure of one atmosphere. These changes are necessary and sufficient for the evaluation of the energy change accompanying cell action. Indeed, the third is usually negligible.

Since, according to the first law, the increase in energy is equal to the algebraic sum of the work and heat effects received by the system, we obtain

$$d\epsilon = (V' - V'')de + dQ + dW_G + dW_P, \quad (1)\ [691]$$

in which $d\epsilon$ is the increment in internal energy of the cell, de is the quantity of electricity which passed through the cell, and V' and V'' the electrical potentials of leads of the same kind of metal attached to the electrodes. Therefore, $(V' - V'')de$ is the electrical work necessary to charge the cell reversibly, dQ is the heat absorbed from external bodies, dW_G is the work done by gravity upon the cell, and dW_P, the work done upon the cell when the volume changes. Since no current is flowing, $(V'' - V')$ equals the electromotive force, $\pm E$, of the cell.*

Since all changes are to be reversible, dQ will be transferred to or from the cell under conditions of thermal reversibility, that is to say, the cell at every instant must be at the same temperature as the external source from which it receives the heat or by which the heat is withdrawn. This is the only source of change of entropy, and since the above condition of reversibility prevails, the increment in entropy at constant temperature will be

$$d\eta = \frac{dQ}{t}. \quad (2)\ [692]$$

The first and second laws, therefore, lead to the equation for the energy increment of the cell,

$$d\epsilon = (V' - V'')de + td\eta + dW_G + dW_P, \quad (3)\ [693]$$

or the equation for the electromotive force,

$$(V'' - V') = -\frac{d\epsilon}{de} + \frac{td\eta}{de} + \frac{dW_G}{de} + \frac{dW_P}{de}. \quad (4)\ [694]$$

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* Two conventions regarding the sign of electromotive force are in use. For a given direction of the current through the cell its electromotive force is $V'' - V'$ or $V' - V''$ according to the convention which we adopt. Since this is largely a matter of personal preference, the adoption of one convention or the other will add nothing to the present general development. Therefore, we shall write $\pm E$ for the electromotive force.

If the cell actually discharges at a finite rate, the conditions of reversibility no longer prevail, and the cell is no longer a thermodynamically useful "perfect electrochemical apparatus." On the other hand, if the cell is maintained at constant temperature, we have, in general,

$$d\eta \geqq \frac{dQ}{t} \qquad (5)\ [695]$$

and, therefore, for the electrical work done by the cell,

$$(V'' - V')de \leqq -d\epsilon + td\eta + dW_G + dW_P. \qquad (6)\ [696]$$

Before proceeding to further discussion of these equations, we shall consider the relation of the reversible electrical work to the work content function ψ and the thermodynamic potential ζ (Gibbs, I, 349). The definition of ψ is given by the equation

$$\psi = \epsilon - t\eta, \qquad (7)\ [87]$$

and, therefore, at constant temperature,

$$d\psi = d\epsilon - td\eta. \qquad (8)$$

If this value of $(d\epsilon - td\eta)$ be substituted in equations (4) and (6), we obtain

$$(V'' - V') = -\frac{d\psi}{de} + \frac{dW_G}{de} + \frac{dW_P}{de} \qquad (9)\ [697]$$

for the electromotive force of a reversible cell and

$$(V'' - V')de \leqq - d\psi + dW_G + dW_P \qquad (10)\ [698]$$

for the electrical work of any cell at constant temperature.

The value of the term due to gravity is extremely small, and negligible in ordinary cells. Further, dW_P is the reversible work done on the cell corresponding to the volume contraction or expansion against a pressure p, and is equal to $-pdv$. Hence, for the reversible cell at constant temperature,

$$(V'' - V')de = -d\psi - pdv, \qquad (11)$$

which, at constant volume and temperature, becomes simply

$$(V'' - V')de = -d\psi. \tag{12}$$

Thus, if the cell is maintained at constant volume and temperature, the reversible electrical work done by cell discharge equals the decrease in work content.

In actual experimental studies, we are more likely to be concerned with processes at constant pressure and temperature, and for this reason Gibbs' thermodynamic potential ζ is of extraordinary usefulness. This function is defined by

$$\zeta = \epsilon - t\eta + pv \qquad (13)\ [91]$$

and, consequently, at constant pressure and temperature, an increment in ζ is given by

$$d\zeta = d\epsilon - td\eta + pdv. \tag{14}$$

Since equation (4) [694] may be written

$$V'' - V' = \frac{-d\epsilon + td\eta - pdv}{de} \tag{15}$$

if we neglect dW_G, we immediately obtain for the reversible cell,

$$(V'' - V')de = -d\zeta, \qquad (16)\ [699]$$

and for any cell,

$$(V'' - V')de \leqq -d\zeta. \qquad (17)\ [700]$$

The reversible electrical work at constant pressure and temperature is equal to the decrease in thermodynamic potential due to the chemical reaction taking place in the cell. This equation is of great importance since it affords a method of evaluating directly the changes of thermodynamic potential in many chemical reactions which otherwise could not readily be obtained.

These few considerations, deductions, and equations represent Gibbs' explicit contribution to the thermodynamic theory of the galvanic cell as contained in the "Equilibrium of Heterogeneous Substances." The directness and simplicity of his method are strikingly manifest.

Let us consider for the moment equation (15), which, allowing for an irreversible process, is

$$(V'' - V')de \leqq -d\epsilon + td\eta - pdv. \tag{15a}$$

If the cell is maintained at constant volume, the last term vanishes, and if no heat is absorbed or evolved by the cell, the term $td\eta$ vanishes, and the electrical work is equal to or less than the diminution of energy. Owing to the lack of very accurate experimental results as well as a confusion regarding the fundamental concepts involved, and to the fact that, in some cases of familiar cells, the term $td\eta$ is small compared to $d\epsilon$, many investigators of the last century were of the opinion that the electrical work is entirely accounted for by the diminution of energy. Since cells are measured at constant temperature and not at constant entropy, there is no reason why the term $td\eta$ should vanish. Gibbs, therefore, takes great care in the subsequent discussion (Gibbs, I, 340–347) to place this matter in the correct light.

We shall postpone the consideration of this matter and consider the alternative deduction of the general law (equation [6]) given in the second letter to the Secretary of the Electrolysis Committee of the British Association for the Advancement of Science (Gibbs, I, 408–412). Gibbs wrote this letter in order to explain more fully his position, and its contents constitute the only other explicit statement of his thermodynamics of the galvanic cell.

Consider a reversible cycle in which a cell discharges at a constant temperature t', producing electrical work, mechanical work and possibly heat effects. Chemical changes will take place. Then, by reversible processes which do not involve the passage of electricity, bring the system back to its original state by supplying or withdrawing the necessary work and heat.

Let W and Q equal the work done and the heat absorbed by the system during the discharge of the cell, and $[W]$ and $[Q]$ equal the corresponding work and heat changes during the reversible processes employed to bring the cell back to its original state. Since by the first law of thermodynamics the algebraic sum of the work and heat effects in a cycle is zero,

$$W + Q + [W] + [Q] = 0. \quad (18) \; ([1] \text{ p. } 408)$$

By the second law the algebraic sum of the entropy changes throughout such a cycle is zero. Hence, we obtain

$$\frac{Q}{t'} + \int \frac{dQ}{t} = 0, \qquad (19) \; ([2] \text{ p. } 408)$$

where t' is the temperature at which the cell charges or discharges. In the reverse process, the heat is supplied or withdrawn throughout a range of temperatures.

If we neglect the term due to gravity, the reversible work during cell discharge involving the passage of one unit of electricity is

$$W = (V' - V'') + W_P. \quad (20) \; ([3] \text{ p. } 409)$$

From equations (18), (19), and (20) we readily obtain

$$V'' - V' = W_P + [W] + [Q] - t' \int \frac{dQ}{t}. \quad (21) \; ([4] \text{ p. } 409)$$

$[W] + [Q]$ is the increase in energy $\Delta\epsilon$, supplied in bringing the cell back to its original condition, and this by the first law is equal numerically, but opposite in sign to the decrease in energy, $-\Delta\epsilon$, during cell discharge. Further, $\int \frac{dQ}{t}$ is the entropy change during the reverse process, and is equal, but opposite in sign, to the entropy change $\Delta\eta$ during discharge. Therefore,

$$V'' - V' = -\Delta\epsilon + t'\Delta\eta + W_P. \quad (22) \; ([5] \text{ p. } 409)$$

Since the variables of equation (15) are all extensive, it may be integrated term by term to give equation (22).

Let us now define a temperature t'', such that

$$\frac{[Q]}{t''} = \int \frac{dQ}{t}, \qquad (23) \; ([7] \text{ p. } 410)$$

which shows how, by means of a reversible process, the heat $[Q]$ absorbed at constant temperature t'' may replace that absorbed at a series of temperatures denoted by t. The temperature t'' is the highest at which *all* the heat may be supplied to the system. Eliminating $\int \frac{dQ}{t}$ from equation (21) by means of equation (23), we obtain

$$V'' - V' = \frac{t'' - t'}{t''}[Q] + [W] + W_P. \qquad (24)\ ([6]\ \text{p.}\ 410)$$

This equation can be derived from the usual form of reversible cycle in which the cell is discharged isothermally at t', heated to t'', then the changes produced reversed isothermally at t'' without the flow of electricity, and finally cooled to t'. The above equation would be true for such a process if the heat absorbed during the heating from t' to t'' cancelled that evolved during the cooling from t'' to t'. This may not be true for a specific case, but if we define t'' by equation (23), then equation (24) is strictly valid. We shall find later that this definition considerably simplifies theoretical discussion.

The remainder of the letter which we have been discussing is devoted to showing that the equations developed are in accord with those derived by Helmholtz. Gibbs proceeds to deduce the equation of Helmholtz,

$$\frac{dE}{dt} = -\frac{Q}{t}, \qquad (25)\ ([11]\ \text{p.}\ 411)$$

by simple transformations of equation (22), and thus shows that his methods lead to the same conclusions as those of this investigator.

II. On the Question of the Absorption or Evolution of Heat during Galvanic Cell Processes

As we have shown by consideration of equation (15), there is every reason to believe that during charging or discharging of a galvanic cell at constant temperature, heat may be absorbed or evolved. Gibbs uses three lines of argument to show the error made in neglecting these heat changes. The first depends upon the conception of a cell at constant volume, or "in a rigid envelop," which, during charge or discharge, does not change in intrinsic energy. In this case, the reversible electrical work performed by the cell is equal to the heat absorbed. The second argument depends on the theoretical conclusion that unless a reaction can produce all its heat at an infinitely high temperature the reversible electrical work cannot equal the decrease in energy. The third argument is empirical. Gibbs computes, from the best data obtainable at that time, the values of the electrical work, change of energy, and heat absorbed, and shows that the heat term $t d\eta$ always exists and is sometimes very considerable. We shall consider these arguments in turn.

That it is possible to construct a cell such that

$$(V'' - V')de \leqq t d\eta \tag{26}$$

is easily shown. Consider two hydrogen electrodes in two limbs of a U-tube. Let the pressure on a large constant volume of hydrogen on the left side be two atmospheres and the pressure on a large constant volume of hydrogen on the right side be one atmosphere. This difference in pressure is compensated for by the difference in heights between the columns of hydrochloric acid in the two limbs. If we neglect the small effect of gravity, the net effect of the cell reaction will be

$$H_2 \text{ (2 atm.)} \rightarrow H_2 \text{ (1 atm.)}$$

at constant volume and temperature. Since there is no increase or decrease in energy in the above process provided that hydrogen is a perfect gas, and since the term $p dv$ vanishes, the reversible electrical work will equal $t d\eta$. This may be more concisely stated by equation (12) whereby

$$(V'' - V')de = -d\psi]_{v,t} = -d\epsilon + t d\eta = t d\eta,$$

since there is no energy change.

Gibbs now proceeds to show that the absorption or evolution of heat is a usual phenomenon accompanying galvanic cell action at constant temperature. He asks us to consider a change in which two molecules, A and B, combine to form a third, AB, with the evolution of heat Q. Now imagine them to react in a galvanic cell at a temperature t', and then complete a cycle by bringing the system back to its initial state by a series of reversible processes which involve the supplying of heat, but which for the sake of simplicity involve no work. This cycle can be represented by

$$A + B \rightarrow AB + W + Q \qquad (t = t')$$

$$A + B \leftarrow AB + [Q] \qquad (t = t'')$$

in which the intrinsic energy changes are $\Delta\epsilon = [Q]$ at t'', and $-\Delta\epsilon = W + Q$ at t', respectively. According to equation (19), we have the well known relation

$$\frac{Q}{t'} + \frac{[Q]}{t''} = 0, \tag{27}$$

where t'' is defined by equation (23), and equals the highest temperature at which *all* the heat may be obtained. Obviously, if $[Q]$ exists and possesses a finite value at a finite temperature, Q must exist at a temperature, t'. Since a change in a finite quantity of substance will be accompanied by a finite change in internal energy, $[Q]$, the only condition which will cause Q to vanish will be that under which all the heat may be obtained at an infinite temperature. Gibbs does not deny this possibility, but simply states that this certainly does not represent the usual case. Further, the magnitude of Q is given by $\frac{t'}{t''}[Q]$, and the work performed by the cell, W, is given by $\frac{t'' - t'}{t''}[Q]$. These considerations form the basis of the discussion on pp. 342–344 of the "Equilibrium of Heterogeneous Substances," and in the first letter (Gibbs, I, 406) to the Secretary of the British Association for the Advancement of Science.

The remainder of the discussion of this subject on pp. 344–348 of the "Equilibrium of Heterogeneous Substances" has simply to do with proving that the data which existed at the time of writing, and which were obtained chiefly by Favre, substantiated the existence of heat changes during cell action. Since a great many accurate observations obtained in recent years completely confirm the contentions of Gibbs, and since the illustrations employed by him are far less accurate, it seems unnecessary to discuss this matter further.

III. The Extension of the Theory of Galvanic Cells Not Explicitly Developed, but Contained Implicitly in the Thermodynamics of Gibbs

Equation (17) [700] has proved to be of the greatest importance to chemistry, and since the ζ function is peculiar to Gibbs it is to this extent unique in the history of the subject. This equation states that the reversible electrical work obtainable from a cell at constant temperature and pressure is equal to the decrease $-d\zeta$, in thermodynamic potential, corresponding to the cell processes. Since it is far more convenient to measure a cell at constant pressure and temperature than at constant volume and temperature, $d\zeta$ is more easily obtainable than $d\psi$.

If then a reversible cell can be constructed in such a way that the net effect of all the changes in the cell during the flow of current corresponds to a chemical reaction, the change in thermodynamic potential may be computed. This affords a very powerful experimental method for investigating the increase or decrease of thermodynamic potential corresponding to reactions which occur between solids, between solids and liquids, or between solids, liquids, and gases. In fact, in recent years cells have been constructed by means of which the changes in thermodynamic potential of all types of chemical reactions have been studied.*

Early in the "Equilibrium of Heterogeneous Substances," Gibbs has shown that the differential of the thermodynamic potential, $d\zeta$, of a phase of variable composition is given by

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* Recent surveys and discussion of this subject may be found in Taylor, *Treatise on Physical Chemistry*, 2nd Ed., Vol. I, pp. 731–745, D. Van Nostrand Company, New York (1924). See also *International Critical Tables*, Vol. VI, pp. 312–340, McGraw-Hill Book Co. (1930).

$$d\zeta = -\eta dt + vdp + \mu_1 dn_1 + \mu_2 dn_2 \ldots + \mu_n dn_n, \tag{28}$$

an equation which is equivalent to equation [92] (Gibbs, I, 87) if n_1, n_2, etc., are the numbers of mols of the components, respectively, and μ_1, μ_2, etc., are the partial derivatives of ζ with respect to n_1, n_2, etc.

From this we immediately find that, at constant composition,

$$\left.\frac{d\zeta}{dt}\right]_p = -\eta, \tag{29}$$

and

$$\left.\frac{d\zeta}{dp}\right]_t = v. \tag{30}$$

Further, from the fundamental equation relating ζ to χ, the heat content function, we obtain

$$\zeta = \chi - t\eta = \chi + t\left.\frac{d\zeta}{dt}\right]_p. \tag{31}$$

From equation (17) we obtain for a reversible cell at constant temperature and pressure the equation

$$d\zeta = \pm Ede. \tag{32}$$

As long as the various phases of the cell are sufficiently large so that their compositions will not be appreciably altered by the flow of a finite quantity of electricity e, then E will remain independent of e, and equation (32) may be integrated. Let us choose the path of integration to correspond with a chemical equation involving a flow of N faradays. Let us denote the faraday by F and employ the subscripts 1 and 2 to refer to the states of the system before and after the process represented by the given chemical equation. Further, let the symbol Δ denote the increase in the value of a function during the given finite process. We obtain

$$\Delta\zeta = \zeta_2 - \zeta_1 = \int_1^2 d\zeta = \pm\int_0^{NF} Ede = \pm NEF. \tag{33}$$

Therefore $\Delta\zeta$ for the chemical reaction involving quantities of reactants and resultants corresponding to the passage of 96,500 coulombs or any multiple thereof may be measured at constant pressure and temperature. If E is expressed in volts, $\Delta\zeta$ is in joules. Substituting this value of $\Delta\zeta$ in equations (29), (30), and (31), we obtain

$$\pm \left.\frac{d(NEF)}{dt}\right]_p = \Delta\eta, \tag{34}$$

$$\pm \left.\frac{d(NEF)}{dp}\right]_t = \Delta v, \tag{35}$$

where $\Delta\eta$ and Δv denote the finite changes of entropy and volume respectively in the cell reaction, and

$$\pm NEF = \Delta\chi \pm t \left.\frac{d(NEF)}{dt}\right]_p. \tag{36}$$

Thus, not only do we obtain the pressure and temperature coefficients of electromotive force, but also the important equations by means of which the changes of entropy and heat content of chemical reactions can be obtained from measurements of E. Equation (34) is equivalent to equation (25). This method of measuring the entropy change in a reaction has proved to be of great importance in obtaining the data necessary for the verification of the so-called "third law of thermodynamics."*

Let us now consider two cells which are to be measured at constant pressure and temperature:

$$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm.}) \mid \mathrm{HCl}(m_1) \mid \mathrm{AgCl} \mid \mathrm{Ag};\quad \pm E_1,$$

and

$$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm.}) \mid \mathrm{HCl}(m_2) \mid \mathrm{AgCl} \mid \mathrm{Ag};\quad \pm E_2,$$

and their corresponding reactions,

$$\tfrac{1}{2}\mathrm{H_2}\ (1\ \mathrm{atm.}) + \mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{HCl}(m_1),$$

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* Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, Chapter XXXI, McGraw-Hill Book Co., New York (1923).

and

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + \text{AgCl} \rightarrow \text{Ag} + \text{HCl}(m_2).$$

By combining these cells we obtain the very important concentration cell without liquid junction,

$$\text{Ag} \mid \text{AgCl} \mid \text{HCl}(m_2) \mid H_2 \mid \text{Pt} \mid H_2 \mid \text{HCl}(m_1) \mid \text{AgCl} \mid \text{Ag};\quad \pm(E_1 - E_2),$$

to which will correspond the cell process

$$\text{HCl}(m_2) \rightarrow \text{HCl}(m_1).$$

This means that the sum of all the changes occurring in this cell during the passage of the current is the transfer of hydrochloric acid from a solution at a concentration m_2 to one at a concentration m_1. In other words, the process may be regarded as the reversible removal of one mol of hydrochloric acid from an infinite quantity of solution at a concentration m_2, and its addition to an infinite quantity of solution at a concentration m_1. The reversible electrical work will be $\pm(E_1 - E_2)F$.

According to equation [104] (Gibbs, I, 89), the chemical potentials of the components of a phase are

$$\mu_1 = \left.\frac{\partial \zeta}{\partial n_1}\right]_{p,\,t,\,n_2,\,\cdots\,n_n},\ \mu_2 = \left.\frac{\partial \zeta}{\partial n_2}\right]_{p,\,t,\,n_1,\,n_3,\,\cdots\,n_n},\ \text{etc.}\qquad (37)\ [104]$$

This formula refers to the change in ζ for an infinitesimal change of composition in a finite phase. Correspondingly we have for a finite change of composition in an infinite phase

$$\mu_1 = \left.\frac{\Delta \zeta}{\Delta n_1}\right]_{p,\,t,\,n_2,\,\cdots\,n_n},\ \mu_2 = \left.\frac{\Delta \zeta}{\Delta n_2}\right]_{p,\,t,\,n_1,\,n_3,\,\cdots\,n_n},\ \text{etc.}\qquad (38),$$

where the operator Δ refers to the change in value of a function or a variable in a finite process. Thus, if we add one gram of component 1 to a very large quantity of the solution under the conditions specified by the subscripts, μ_1 will equal the increase in ζ of the phase. If the unit of mass is the mol, μ_1 will equal the corresponding increase in total thermodynamic potential upon the addition of one mol.

With this fundamental consideration in view, it immediately becomes clear that the reversible electrical work of the cell without liquid junction just described measures the change in thermodynamic potential when one mol of hydrochloric acid at a concentration m_2 is removed from one solution and then added to the solution at a concentration m_1. Therefore, for the transfer of one mol of acid, we obtain by (38)

$$\mu_1' - \mu_1'' = \Delta\zeta = \pm F(E_1 - E_2). \tag{39}$$

These considerations show that the measurements of electromotive forces of reversible cells containing various electrolytes of the same or different valence types afford direct measurements of the changes in chemical potentials of ionized components with their concentrations. Further, by measurements of the temperature coefficients of electromotive forces of cells of this type, and by employing the fundamental equations (34) and (36), the corresponding changes $\Delta\chi$ of heat content, as well as of entropy may be determined. Further, by equation [97] (Gibbs, I, 88) the chemical potential of one component, the solvent for example, may be computed from that of the solute, or *vice versa.* Therefore, since we may measure the chemical potential of the solute from cell measurements, we may compute that of the solvent. In this way we may relate the electromotive force of a cell with the lowering of the vapor pressure, the lowering of the freezing point, and the osmotic pressure of the solution.

Since the development of both the experimental side and the theory of the physical chemistry of solutions has depended to a considerable extent upon the evaluation of the chemical potentials, the value of this powerful and direct method of measurement of these quantities cannot be overestimated.*

IV. Developments of Importance to the Theory of the Physical Chemistry of Solutions since Gibbs

The general thermodynamics of Gibbs is complete and affords a basis for the exact treatment of the problems which have arisen. Consequently, any further advance must rest upon some extra-thermodynamical discovery, for example, some empirical law. We have found that by a suitable mechanism, we may obtain the change in chemical potential of an ionizing component from the study of a process represented by

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* A more detailed and systematic presentation of recent work on this subject is given by Harned in Taylor's *Treatise on Physical Chemistry,* Chap. XII.

$$\mathrm{HCl}(m_2) \rightarrow \mathrm{HCl}(m_1).$$

If we let m_2 vary and keep m_1 constant, at unit value, or at an arbitrary standard value, then we can measure the change in the quantity, $\mu_1' - \mu_1''$, with the concentration. If this is done, we find that as m_2 approaches zero, μ_1'' changes with the concentration at constant temperature according to the law

$$\mu_1' - \mu_1'' = 2Rt \log \frac{m_1}{m_2},$$

or, since both μ_1' are 2 $Rt \log m_1$ are fixed,

$$\mu_1'' = 2Rt \log m_2 + I, \tag{40}$$

where I is a function of t and p only. Since the electrical process involves the transfer of both hydrogen and chloride ions, the factor 2 occurs in the expression on the right. This is the form of the expression derived from the perfect gas laws. It is, therefore, the equivalent of van't Hoff's law for dilute electrolytes. This experimental discovery of van't Hoff, coupled with the ionic theory of Arrhenius, marked the beginning of a very extended experimental investigation of solutions of electrolytes. As a result, it was soon found that, in the cases of solutions of strong electrolytes, wide departures from this law occur.

Without any addition to the fundamental thermodynamic theory, we may numerically overcome this difficulty by inserting a term which serves to measure the deviation from van't Hoff's law. Thus,

$$\mu'' = 2Rt \log a_{\pm} + I = Rt \log a_{\mathrm{H}} a_{\mathrm{Cl}} + I,$$

or

$$\mu'' = 2Rt \log m_2 + 2Rt \log \gamma + I, \tag{41}$$

where $a_{\mathrm{H}}a_{\mathrm{Cl}}$ is the activity product of the ions as defined by Lewis,* and γ, or $\frac{a_\pm}{m}$, is the activity coefficient. Hydrochloric acid is a uni-univalent electrolyte and, consequently, the reaction of this cell represents the transfer of one gram ion of hydrogen ion and one gram ion of chloride ion. The modifications necessary for the general treatment of electrolytes of different valence types can easily be made. Consider any strong electrolyte at a molal concentration, m, which dissociates according to the scheme

$$C_{\nu_+}A_{\nu_-} = \nu_+C + \nu_-A,$$

and let

$$\nu = \nu_+ + \nu_-,$$

$$a_2 = a_+^{\nu_+}\, a_-^{\nu_-},$$

where a_+ and a_- are the activities of the cation and anion, respectively, and a_2, defined by the above equation, may be regarded as the activity of the electrolyte, and

$$a_\pm = (a_+^{\nu_+}\, a_-^{\nu_-})^{\frac{1}{\nu}}.$$

Then equation (41) may be written in general

$$\mu = Rt \log a_2 + I = \nu Rt \log a_\pm + I, \tag{42}$$

which serves to define the activity. I is a function of the pressure and temperature, but not of the concentrations of the solute epecies. Further, we define the activity coefficient of any electrolyte by

$$\gamma = \frac{a_\pm}{(\nu_+^{\nu_+}\, \nu_-^{\nu_-})^{\frac{1}{\nu}} m}, \tag{43}$$

and always measure it in reference to a value of unity when m equals zero.

By means of cell measurements we obtain μ in reference to an arbitrary standard state, and, therefore, $a_\pm$ may also be obtained. Now γ may be computed if we let m be the molal concentration of the electrolyte. This is purely arbitrary since the molal concentration of the electrolyte tells us nothing regarding the real concentrations of the ions in the solution. The activity coefficient γ, however, acquires an important physical significance if the real ionic concentrations are known.

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* Lewis, *Proc. Am. Acad.*, **37**, 45 (1901); **43**, 259 (1907).

According to the classical theory of Arrhenius, γ was thought to measure the actual degree of dissociation of an electrolyte. Later, it was called by Lewis "the thermodynamic degree of dissociation". If this quantity measures the degree of dissociation, then the law of mass action in its classic form should be applicable to all classes of electrolytes. In the case of strong electrolytes, this conclusion was found to be erroneous, and therefore the first suppositions regarding γ were entirely incorrect. The difficulty resides in the failure of these early theories to take into account the effects of the attractive and repulsive forces between the ions, which for charged particles vary inversely as the square of the distance. The careful consideration of these effects constitutes the departure of the recent developments of the theory of solutions from the classical theory.

The most fruitful advance has come from the assumption that, in moderate concentrations in a solvent of high dielectric constant, the strongest electrolytes are completely dissociated into ions. Thus m in the cases of hydrochloric acid solutions, sodium chloride solutions, etc., is the true ionic concentration. If this is true, γ acquires a definite physical significance. Further, if the assumption of complete dissociation is correct, then γ must be calculable from fundamental considerations regarding the forces of attraction and repulsion between the ions.

The various attempts to solve this problem have culminated in the theory of Debye and Hückel.* By the skillful application of Poisson's equation to a system of charged particles in thermal motion, they have succeeded in proving that in moderately dilute solutions γ is a function of the electrostatic forces.

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* Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

Since their calculation of γ is numerically a very close approximation, it justifies their initial assumption of complete dissociation of strong electrolytes. Even a conservative estimate of this theory will convince us that by far the larger part of the deviation factor, γ, is due to interionic forces in the case of strong electrolytes in media of high dielectric constant, such as water. It would be far beyond the purpose of the present discussion to develop this theory and its many ramifications, but the knowledge that m is an ionic concentration or very nearly so in the case of strong electrolytes permits us to develop the possibilities of the study of reversible cells to a considerable extent without any sacrifice in accuracy.

We shall now sketch briefly some developments which illustrate the more recent means of obtaining valuable data regarding strong electrolytes, weak electrolytes, and ampholytes from reversible cell measurements. To assure exactness, we shall omit measurements of all cells with liquid junctions since these all involve an undefinable and physically meaningless liquid junction potential.*

(1) *The Activity Coefficients of Strong Electrolytes*

We have already shown how the change in chemical potential of hydrochloric acid in passing from a solution at one concentration to a solution at another concentration may be measured by a cell without liquid junction. For the change

$$CA(m_2) \rightarrow CA(m_1),$$

we have, according to equation (42),

$$-\Delta\zeta = (\mu' - \mu'') = Rt \log \frac{a_C' a_A'}{a_C'' a_A''}. \qquad (44)$$

If we adopt the convention that a positive electromotive force accompanies a decrease in thermodynamic potential, we obtain from equation (39)

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* Harned, *J. Physical Chem.*, **30**, 433 (1926). Taylor, *J. Physical Chem.*, **31**, 1478 (1927). Guggenheim, *J. Physical Chem.*, **33**, 842 (1929); **34**, 1540 (1930).

$$NEF = Rt \log \frac{a_C'a_A'}{a_C''a_A''},$$

or

$$E = \frac{2Rt}{NF} \log \frac{\gamma' m_1}{\gamma'' m_2}. \tag{45}$$

Thus, ifwe know γ at one concentration, we may compute it at another. The activity coefficient, however, is always computed in reference to unity at infinite dilution. If we let E_0 equal the electromotive force of the cell when $\gamma_1' m_1$ equals unity, and refer all values of E and $\gamma'' m_2$ to this standard value, we obtain

$$E - E_0 = -\frac{2Rt}{NF} \log \gamma'' - \frac{2Rt}{NF} \log m_2 \tag{46}$$

or

$$E + \frac{2Rt}{NF} \log m_2 = E_0 - \frac{2Rt}{NF} \log \gamma''. \tag{47}$$

Since γ'' is taken to be unity as m_2 equals zero, the left-hand member of the equation (at zero concentration) equals the normal electrode potential, E_0. By plotting the left-hand member against a convenient function of the concentration, E_0 may be evaluated, and subsequently γ may be calculated by equation (47) at any concentration, m_2, at which E is known. Such a method permits the determination of γ at a constant temperature from electromotive force data only.

In recent years the activity coefficients of many electrolytes have been determined by measurements of cells of this type. If we replace the hydrochloric acid by a halide of an alkali metal and the hydrogen electrode by a dilute alkali metal amalgam, the cell,

$$\text{Ag} \mid \text{Ag}X \mid MX(m_2) \mid M_x\text{Hg} \mid MX(m_1) \mid \text{Ag}X \mid \text{Ag},$$

is formed. The electromotive force of this cell measures the change of thermodynamic potential corresponding to the reaction

$$MX(m_2) \rightarrow MX(m_1),$$

whence μ'' and μ' may be determined.*

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* MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915). MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920). Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926). Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).

Further, we mention the cell,

$$H_2 \mid MOH(m_2) \mid M_xHg \mid MOH(m_1) \mid H_2,$$

which measures the transfer corresponding to

$$MOH(m_2) + H_2O(m_1) \rightarrow MOH(m_1) + H_2O(m_2),$$

whence the activity coefficients of alkali metal hydroxides may be measured. By other cells of the same types, alkali metal sulphates and alkaline earth chlorides have been studied. All these data have an important bearing on the theory of electrolytic solutions.*

Not only may we obtain these changes in chemical potentials for single electrolytes by these measurements, but also the chemical potentials of one electrolyte in a solution containing another electrolyte may be computed. From the cell,

$$Ag \mid AgX \mid HX(m_1),\ MX(m_2) \mid H_2 \mid HX(m) \mid AgX \mid Ag,$$

we may measure the change of thermodynamic potential of a halide acid from the solution containing the chloride to the pure acid solution, which we represent by

$$HX(m_1)\ [MX(m_2)] \rightarrow HX(m).$$

Thus, we may obtain the activity coefficient of the acid at a concentration (m_1) in a salt solution of a concentration (m_2). Suffice it to say that by similar cells we now know the value of this important quantity for hydrochloric acid, sulphuric acid, and hydrobromic acid in many salt solutions.† Further, cells of the type,

$$H_2 \mid MOH(m_1),\ MX(m_2) \mid M_xHg \mid MOH(m) \mid H_2,$$

permit the calculation of the activity coefficients of hydroxides in salt solutions.‡

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* Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923). Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925). Harned and Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926).

† Harned, *J. Am. Chem. Soc.*, **38**, 1986 (1916); **42**, 1808 (1920). Harned and Akerlöf, *Physik. Z.*, **27**, 411 (1926).

‡ Harned, *J. Am. Chem. Soc.*, **47**, 684 (1925).

(2) *The Activity Coefficients of Weak Electrolytes in Salt Solutions*

(*a*) *The Ionic Activity Coefficient of Water in Salt Solutions.* We have described a cell by means of which the activity coefficient of hydrochloric acid may be obtained in a chloride solution. Suppose we maintain $(m_1 + m_2)$ constant and measure γ in the solutions of varying acid and salt concentration. It is found that γ varies with the acid concentration according to the law*

$$\log \gamma = \alpha m_1 + \log \gamma_0. \tag{48}$$

Thus at constant total molality γ extrapolates to γ_0 at zero concentration of acid, whence we know $\gamma_H\gamma_{Cl}$ in the salt solution which is free from acid. In a similar manner from measurements of the cells containing sodium hydroxide in the sodium chloride solutions, we may obtain $\frac{\gamma_{Na}\gamma_{OH}}{a_{H_2O}}$ in the hydroxide-free salt solution. Also, from measurements of the cells containing sodium chloride, we know $\gamma_{Na}\gamma_{Cl}$ at the concentration $(m_1 + m_2)$. Therefore, if we multiply $\gamma_H\gamma_{Cl}$ by $\frac{\gamma_{Na}\gamma_{OH}}{a_{H_2O}}$ and divide by $\gamma_{Na}\gamma_{Cl}$, we obtain the ionic activity coefficient product of water, $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$, at this concentration of salt. Obviously, by this method, $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ may be obtained at other salt concentrations.

The primary dissociation of water is represented by

$$H_2O \rightleftharpoons H^+ + OH^-,$$

and the thermodynamic dissociation constant, K, is given exactly by

$$K = \frac{a_H a_{OH}}{a_{H_2O}} = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} m_H m_{OH}. \tag{49}$$

Since we may determine $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ in the salt solutions, the classical dissociation product, $m_H m_{OH}$, may be determined if we know K, and in this way we may study the effects of electrolytes on the dissociation of the solvent.*

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* Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926). Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

We have still to determine K from the electromotive forces of cells without liquid junction. Consider the cell,

$$H_2 \mid MOH(m_1),\ MCl(m_2) \mid AgCl \mid Ag.\dagger$$

Its electromotive force at 25° is given by

$$E = E_0 - 0.05915 \log_{10} m_H m_{Cl} - 0.05915 \log_{10} \gamma_H \gamma_{Cl}, \quad (50)$$

where E_0 may be obtained from the cell containing hydrochloric acid. If we substitute the value of m_H obtained from equation (49), we obtain

$$\begin{aligned} E &= E_0 - 0.05915 \log_{10} \frac{K a_{H_2O} m_{Cl}}{\gamma_H \gamma_{OH} m_{OH}} - 0.05915 \log_{10} \gamma_H \gamma_{Cl} \\ &= E_0 - 0.05915 \log_{10} K - 0.05915 \log_{10} \frac{\gamma_H \gamma_{Cl} a_{H_2O}}{\gamma_H \gamma_{OH}} \\ &\qquad - 0.05915 \log_{10} \frac{m_{Cl}}{m_{OH}}. \qquad (51) \end{aligned}$$

E_0 is known. In dilute solutions the third term on the right is very close to unity since it contains the ratio of activity coefficient products. Therefore,

$$E + 0.05915 \log_{10} \frac{m_{Cl}}{m_{OH}}$$

in very dilute solutions has very nearly a constant value. Thus, the extrapolation of this quantity to zero ionic concentration is a simple matter, and its value at infinite dilution is equal to $[E_0 - 0.05915 \log_{10} K]$. We have, therefore, an independent measure of K.

(b) *The Ionic Activity Coefficients and Dissociation of Weak Acids and Bases in Salt Solutions.* By the application of the principles just discussed, very important information concerning weak acids and bases in solvents containing salt solutions may be obtained. We shall consider the acid case only, since the bases may be investigated in exactly the same manner. Let us construct the cell,

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* Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925).

† Roberts, *J. Am. Chem. Soc.*, **52**, 3877 (1930).

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(m_1),\ M\mathrm{Cl}(m_2) \mid \mathrm{H_2} \mid \mathrm{HAc}(m),\ M\mathrm{Cl}(m_3) \mid \mathrm{AgCl} \mid \mathrm{Ag},$$

in which HAc is a weak acid, m_1 is 0.01 molal or less, and the concentrations are such that the total ionic concentration on the two sides is the same or very nearly so, so that $m_1 + m_2 = m_{\mathrm{H}} + m_3$, where m_{H} is the hydrogen ion concentration in the solution of the weak acid. The electromotive force of this cell at 25° is given by

$$E = 0.05915 \log_{10} \frac{\gamma_{\mathrm{H}}'' \gamma_{\mathrm{Cl}}''}{\gamma_{\mathrm{H}}' \gamma_{\mathrm{Cl}}'} + 0.05915 \log_{10} \frac{m_1 m_2}{m_{\mathrm{H}} m_3}, \qquad (52)$$

where the double accent refers to the hydrochloric acid solution and the single accent to the weak acid solution. Since m_1, m_2, and m_3 are known m_{H} may be evaluated if the first term on the right of this equation is known. Two secondary effects influence this term, which can be completely taken into account if sufficient care is exercised. The first and most important is the effect of the presence of the undissociated molecule of the weak acid which causes $\gamma_{\mathrm{H}}'\gamma_{\mathrm{Cl}}'$ to differ from its value in pure water even though the concentrations of the ions in the two cell compartments are the same. The second effect is much simpler and merely requires a knowledge of the activity coefficient of hydrochloric acid in the salt solution. This situation has been investigated very thoroughly by Harned and Robinson, and Harned and Owen, who show that both $\gamma_{\mathrm{H}}''\gamma_{\mathrm{Cl}}''$ and $\gamma_{\mathrm{H}}'\gamma_{\mathrm{Cl}}'$ as well as m_{H} can be determined without the introduction of any inexact considerations.

The dissociation of the acid is represented by

$$\mathrm{HAc} \rightleftharpoons \mathrm{H^+} + \mathrm{Ac^-},$$

and the ionization constant by

$$K = \frac{\gamma_{\mathrm{H}}\, \gamma_{\mathrm{Ac}}}{\gamma_{\mathrm{HAc}}} \frac{m_{\mathrm{H}}\, m_{\mathrm{Ac}}}{m_{\mathrm{HAc}}} = \gamma_A{}^2 \frac{m_{\mathrm{H}}{}^2}{m - m_{\mathrm{H}}} = \gamma_A{}^2 K_c, \tag{53}$$

where m is the original concentration of the weak acid, and γ_A its activity coefficient in the salt solution. Since we determine m_{H}, K_c becomes known at various salt concentrations. We have yet to find its value at infinite dilution or when γ_A equals unity. This can be done very simply by the use of a function which gives the variation of γ with the total ionic concentration, μ, in dilute solutions; namely,

$$\log_{10} \gamma_A{}^2 = -\sqrt{\mu} + \alpha\mu, \tag{54}$$

where α is an empirical constant. If we take the logarithm of equation (53), we obtain

$$\log_{10} K = \log_{10} K_c + \log_{10} \gamma_A{}^2. \tag{55}$$

Substituting for $\log_{10} \gamma_A{}^2$ and rearranging terms, we find that

$$\log_{10} K_c - \sqrt{\mu} = \log_{10} K - \alpha\mu. \tag{56}$$

Therefore, if we plot $[\log_{10} K_c - \sqrt{\mu}]$, which has been determined against μ, we obtain a straight line in dilute solutions, and the value of the function on the left is equal to $\log_{10} K$ when μ equals zero. By this means we have an independent measure of the dissociation constant, the ionic activity coefficient, and dissociation of a weak acid in a salt solution. The same or very similar methods will also afford very valuable evidence concerning similar properties of weak bases, and ampholytes.*

These considerations, although very brief, serve to show the extent and power of the method of cell measurements when applied to the study of all kinds of electrolytes. It would be far beyond the scope of this discussion to treat the various ramifications which would develop upon considerations of the variations of these quantities with temperature and pressure. Suffice it to say that everything comes back to the experimental evaluation of the chemical potentials of electrolytes, which would have been impossible without the fundamental contribution of Gibbs.

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* A thorough discussion of this subject is to be found in the contributions of: Harned and Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928); Harned and Owen, *ibid.*, **52**, 5079 (1930); 52, 5091 (1930); Owen, *ibid.*, **54**, 1758 (1932); Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

Retrospect and Prospect

We have emphasized the completeness and exactness of Gibbs' treatment of the perfect electrochemical apparatus. If we work in the spirit of the original method, then we must eliminate uncertainties inherent in the use of cells such as those containing liquid junction potentials. The invention and use of the concentration cell without liquid junction is an excellent illustration of an exact method of study. However, the power of this experimental method only becomes apparent when we introduce the chemical potentials and develop the general thermodynamics of Gibbs in its relation to such cells. But even this has not been enough. Extra-thermodynamical considerations which must be experimentally verified and finally proved by fundamental electrostatic theory have been required, and will continue to be necessary before the intricate subject of the nature of the ionic state in solutions will be unravelled and explained. But there will be nothing in these modifications to detract from the value of the contribution of the first master of this subject.

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